

# T R I T I U M

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# in the Physical and Biological Sciences

Volume **I**



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TRITIUM IN THE  
PHYSICAL AND BIOLOGICAL SCIENCES

VOL. I.

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PROCEEDINGS SERIES

# **TRITIUM IN THE PHYSICAL AND BIOLOGICAL SCIENCES**

## **I**

PROCEEDINGS OF THE SYMPOSIUM ON  
THE DETECTION AND USE OF TRITIUM IN THE PHYSICAL  
AND BIOLOGICAL SCIENCES

SPONSORED BY  
THE INTERNATIONAL ATOMIC ENERGY AGENCY  
IN CO-OPERATION WITH THE  
JOINT COMMISSION ON APPLIED RADIOACTIVITY  
AND HELD IN VIENNA, 3—10 MAY 1961

INTERNATIONAL ATOMIC ENERGY AGENCY  
VIENNA 1962

TRITIUM IN THE PHYSICAL AND BIOLOGICAL SCIENCES  
IAEA, VIENNA, 1962  
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## FOREWORD

The use of tritium for research in physics, chemistry, biology and hydrology has in recent years become increasingly important. It was for this reason that the first international conference to discuss the progress of new developments was organized by the IAEA in conjunction with the Joint Commission on Applied Radioactivity and held from 3–10 May 1961, in Vienna.

The first five sessions of the Symposium were devoted to the use of tritium in hydrology, physics and chemistry. Special emphasis was laid on the role of tritium as a tracer in hydrology, especially in the study of water movement. The establishment and improvement of counting and detection techniques to facilitate the application of tritium as a tracer was another aspect discussed in this part of the proceedings. Papers were read on the preparation of tritiated compounds and it was generally agreed that further clarification of the mechanism of various techniques, and of the Wilzbach gas exposure technique in particular, would lead to further developments in the synthesis of a number of tritium compounds important in biology. Other papers were concerned with tritium applications to studies of the mechanism of some chemical reactions together with the effects of tritium isotopes.

During the second part of the Symposium the biological applications of tritium and tritiated compounds were discussed. These included general problems connected with the biological uses of tritium and the radiation effects of tritium on living organisms such as viruses, bacteria and cancer cells. The value of tritium in biological studies became apparent because of the ease with which a large number of metabolically active compounds such as hormones, vitamins and other important constituents in the body can be labelled with tritium. Tritium is also a weak beta-emitter and autoradiographies of tissues and single cells containing tritium-labelled compounds allow an excellent localization of the tracer.

The Symposium was attended by some 290 scientists from 27 countries and five international organizations who altogether contributed a total of 67 papers.

The Agency believes that the publications of the proceedings will not only provide information for a wider public but will also help to stimulate further research in the use of tritium.

## EDITORIAL NOTE

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A

DISTRIBUTION OF TRITIUM IN NATURE,  
METHODS OF ENRICHMENT AND  
APPLICATIONS IN HYDROLOGY

(Session I)





## INTRODUCTION

Prof. W. F. LIBBY (United States of America), Chairman of the inaugural session, opened it with the following speech:

Tritium was first discovered in the Cavendish Laboratory by Lord Rutherford and his co-workers, who found that the (d,d) reaction produced tritium. The (d,d) reaction also produces helium-3. It was not known which of these two, helium-3 or tritium, was radioactive. Alvarez at Berkeley established that helium-3 occurred in nature and was stable. He later proved that tritium was radioactive. Lord Rutherford, in one of his last scientific researches, looked for tritium in natural water. He used the method of enrichment which most of us now studying tritium geophysics use, namely, electrolysis to produce heavy water. He then examined his enriched sample for tritium. However, not knowing that tritium was radioactive, he looked for natural tritium with a mass spectrometer and failed to find it. But such is the course of scientific research that the first tritium to be discovered in natural water was found some years later in Lord Rutherford's sample, when a Geiger counter was used instead of a mass spectrometer. Our research at the University of Chicago, which was concerned with the occurrence of tritium in water in nature, began with an examination of Lord Rutherford's sample, and it was found to be intensely radioactive with tritium. The occurrence of tritium in natural waters is now an old story. We are concerned with two epochs: the pre-thermonuclear explosion epoch and the post-thermonuclear explosion epoch or, described differently, the cosmic ray tritium era and the synthetic tritium era. In samples taken before March 1954, the tritium is very largely cosmic ray in origin. Samples taken after that time are, by and large, synthetic, i. e. man-made, in origin, although there is of course some admixture, so that certain samples taken as early as in 1952 can show synthetic tritium while other samples taken now, for example, from 20-year old wine, can show only cosmic ray tritium.



# TRITIUM GEOPHYSICS: RECENT DATA AND RESULTS\*

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## Abstract — Résumé — Аннотация — Resumen

**Tritium geophysics: recent data and results.** Rain waters contain radioactive hydrogen (tritium) because of the bombardment of the atmosphere by the cosmic rays and because of the synthetic production in the atmosphere by thermonuclear explosions. Prior to 1952, the only source of rain tritium was due to cosmic rays and early measurements established the level of the cosmic ray tritium in terrestrial waters.

Since 1952, and particularly since 1954 and up to 1959, the cosmic ray tritium in rain has been overshadowed by synthetic tritium. For example, California rain now averages about 15 to 20 Tritium Units (1 T.U. is 1 T-atom per  $10^{18}$  H-atoms) and the Mississippi River runs at over 100 T.U., whereas it ran at 6 T.U. before. It is now possible to measure tritium more easily and the finer details of many problems which were not resolved by the cosmic ray tritium can now be established.

The turnover time between the oceans and continental water can now be measured more accurately. Comparisons can be made of the surface waters of the oceans in the northern and southern hemispheres which provide the mixing rate between the two hemispheres. It has also been discovered that tritium remains in the stratosphere as long as non-volatile radioactivity such as strontium-90. The measurement of surface ocean water has indicated that there are extensive areas of upwelling off the coast of Southern California.

**Emploi du tritium en géophysique: données et résultats obtenus récemment.** Les eaux de pluie contiennent de l'hydrogène radioactif (tritium) dont une partie provient du bombardement de l'atmosphère par les rayons cosmiques et l'autre s'est formée par synthèse dans l'atmosphère, sous l'effet des explosions thermonucléaires. Avant 1952, les eaux de pluie ne contenaient que du tritium provenant des rayons cosmiques, et les premières mesures qui ont été faites ont établi la concentration de ce tritium dans les eaux terrestres.

Depuis 1952, et notamment entre 1954 et 1959, la quantité de tritium synthétique contenue dans l'eau de pluie a considérablement augmenté par rapport à celle du tritium naturel. Ainsi, en Californie, l'eau de pluie contient maintenant en moyenne de 15 à 20 unités de tritium (1 unité de tritium = 1 atome de tritium pour  $10^{18}$  atomes d'hydrogène) et la teneur en tritium du Mississippi atteint plus de 100 unités, contre 6 auparavant. Il est maintenant possible de mesurer plus facilement la concentration du tritium et de préciser les détails de nombreux problèmes que l'on n'avait pu résoudre à l'aide du tritium provenant des rayons cosmiques.

On peut maintenant mesurer exactement le cycle des échanges entre les eaux des océans et les eaux continentales. En comparant les eaux de surface des océans de l'hémisphère nord et de l'hémisphère sud, il est possible de calculer le taux de mélange des eaux des deux hémisphères. On a également découvert que le tritium séjourne dans la stratosphère aussi longtemps que les corps radioactifs non volatils, comme le strontium-90. La mesure de la teneur en tritium des eaux de surface de l'océan a mis évidence l'existence de mouvements verticaux en de vastes zones au large de la côte de la Californie méridionale.

**Геофизика трития: последние данные и результаты.** Дождевые воды содержат радиоактивный водород (тритий) в результате бомбардировки атомов атмосферы космическими лучами и в результате вызванного термоядерными взрывами

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процесса синтетической генерации в атмосфере. До 1952 года единственным источником содержащегося в дождевой воде трития являлись космические лучи и согласно более ранним измерениям был установлен уровень появившегося таким образом трития в земных водах.

С 1952 года, и в особенности с 1954 года и вплоть до 1959 года, выпадение получающегося от бомбардировки атмосферы космическими лучами трития было мало по сравнению с выпадением синтетического трития. Например, в настоящее время во время дождя в Калифорнии выпадает в среднем от 15 до 20 единиц трития (1 единица трития равняется 1 атом трития на  $10^{18}$  атомов водорода), и река Миссиссиппи несет свыше 100 единиц трития в то время как прежде в ней было до 6 единиц трития. В настоящее время является возможным более легко измерить содержание трития и могут быть установлены более тонкие детали многих проблем, которые не были решены с помощью трития, получающегося от бомбардировки атмосферы космическими лучами.

В настоящее время может быть точно измерено время оборота между океанами и континентальными водами. Могут быть сделаны сравнения степени смешения поверхностных вод океанов в северном и южном полушариях. Было также открыто, что тритий остается в стратосфере также долго, как нелетучие радиоактивные вещества подобно стронцию-90. Измерение, произведенное в поверхностных слоях океанских вод, показало, что имеются обширные районы подъема уровня воды у побережья Южной Калифорнии.

**Empleo del tritio en geofísica: datos y resultados recientes.** El agua de lluvia contiene hidrógeno radiactivo (tritio) originado en el bombardeo de la atmósfera por los rayos cósmicos y producido también sintéticamente como consecuencia de las explosiones termonucleares. Antes del año 1952, el tritio presente en el agua de lluvia tenía como origen exclusivo la mencionada acción de los rayos cósmicos y las primeras mediciones permitieron determinar la cantidad de tritio, producida, por tales rayos, en las aguas del globo terrestre.

A partir de 1952 y especialmente entre los años 1954 y 1959, la proporción de tritio sintético en el agua de lluvia ha ido superando a la proporción debida a los rayos cósmicos. Así, por ejemplo, el contenido de tritio en las aguas pluviales de California oscila, en la actualidad, entre 15 y 20 unidades de tritio (1 unidad de tritio corresponde a 1 átomo de tritio por  $10^{18}$  átomos de hidrógeno) y asciende a unas 100 unidades de tritio en las aguas del río Mississippi, en tanto que anteriormente contenía 6 de esas unidades. Hoy en día la determinación cuantitativa del tritio ofrece menos dificultades, siendo posible aclarar muchos aspectos de una serie de problemas que no era posible resolver partiendo de los datos obtenidos con ayuda del tritio originado por los rayos cósmicos.

Así, se puede ahora medir con exactitud el tiempo de intercambio entre las aguas oceánicas y las aguas continentales. También es posible comparar las aguas superficiales de los océanos del hemisferio Norte con las del hemisferio Sur y deducir la velocidad de mezcla entre las aguas de los dos hemisferios. Del mismo modo, se ha comprobado que el tritio permanece en la estratosfera tanto tiempo como las sustancias radiactivas no volátiles, tales como el estroncio-90. Por otra parte, las mediciones en las aguas superficiales del océano permitieron comprobar la existencia de vastas zonas de corrientes ascendentes a la altura de la costa de la California meridional.

## Introduction

The method of analysis for natural tritium in water described earlier by our group (GROSSE, A. V., JOHNSTON, W. H., WOLFGANG, R. L. and LIBBY, W. F., 1951; KAUFMANN, S. and LIBBY, W. F., 1954; VON BUTTLAR, H. and LIBBY, W. F., 1955; BEGEMANN, F. and LIBBY, W. F., 1957) and by others (BROWN, R. M. and GRUMMITT, W. E., 1956; GILLETI, B. J., BAZAN, F. and KULP, J. L., 1958; SUESS, H. E., 1958; BROWN, R. M., 1960; CARLSTON, W., THATCHER, L. and RHODEHAMEL, E. C., 1960) has been used to measure a selection of recent rain and surface water and ground water samples of geophysical interest — principally hydrological and oceanographic.

The results are given in Table I, and certain salient features are presented in Figs. 1-4.

## Results

RELATIVE STRATOSPHERIC RESIDENCE TIMES FOR WATER VAPOUR AND  $\text{Sr}^{90}$  PARTICLES (SAMPLES FROM E. A. MARTELL)

Fig. 1 shows for Bedford, Massachusetts, the variation in tritium content of the rains throughout 1959 and the spring, summer, and early fall of 1960, together with the average northern hemisphere fallout for  $\text{Sr}^{90}$  during 1959 (LIBBY and PALMER, 1960, Fig. 1). It is immediately clear that during the spring and summer

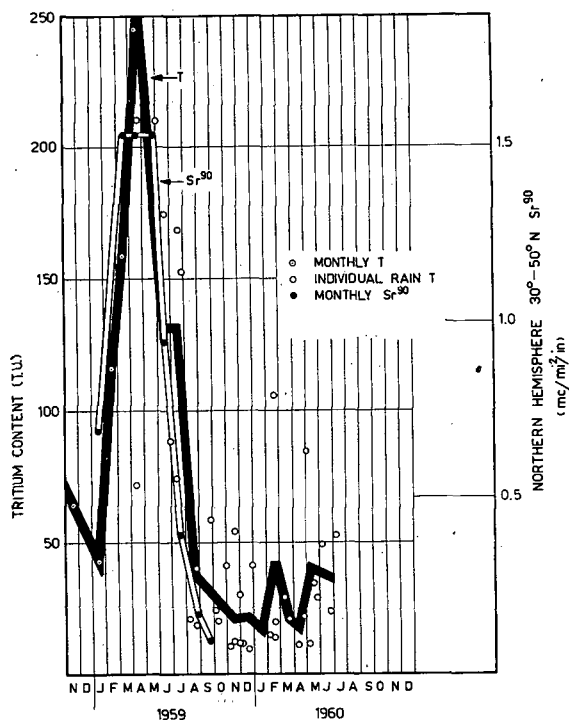


Fig. 1

Bedford tritium in rain vs. northern hemisphere average 30°-50° N Strontium 90 in rain.

of 1959 the peaks attained by the T (Tritium) and  $\text{Sr}^{90}$  fallout rates were proportional to one another with an average proportionality constant of about 130 T.U. (1 Tritium Unit [T.U.] is 1 T-atom/ $10^{18}$  H-atoms) per mc of  $\text{Sr}^{90}$  per square mile per inch of rain or 13 T atoms per  $\text{Sr}^{90}$  atom. Considering that the fallout in the spring and summer of 1959 in the northern hemisphere (LIBBY, 1959; MARTELL, 1959; LIBBY and PALMER, 1960; MARTELL and DREVINSKY, 1960; LOCKHART, 1960) was due largely to the Russian October 1958 test series, this parallelism of the T and  $\text{Sr}^{90}$  fallout strongly suggests that both the T and  $\text{Sr}^{90}$  came from the same source — the island of Novaya Zemla in October 1958 — and that the mechanism of removal from the stratosphere into the troposphere was the same for both T and  $\text{Sr}^{90}$ . Some of the Bedford rains were measured for  $\text{Sr}^{90}$  as well as T, the results being given in Table II (the  $\text{Sr}^{90}$  data were furnished by Dr. E. A. MARTELL and P. J. DREVINSKY of the United States Air Force [Cambridge Research Laboratories]).

TABLE II  
T/Sr<sup>90</sup> RATIO DURING SPRING 1959 PERIODS

Period of Collection	Sr <sup>90</sup> (mc/mi <sup>2</sup> /inch)	T. U.	T/Sr <sup>90</sup> Atoms
Feb. 24 to Mar. 31	0.81 ± .08	159 ± 4	19
Apr. 1 to Apr. 3	0.83 ± .08	292 ± 15	33
May 25 to June 3	0.17 ± .01	220 ± 7	123
July 7 to July 13	0.06 ± .02	74 ± 7	117
			Average 73

The scatter is such that if the correlation shown in Fig. 1 were not so clear, it would be difficult to justify the whole consideration of the T/Sr<sup>90</sup> atomic ratio on the Bedford data alone. This probably is due to the tropospheric precipitation mechanism being different for T and Sr<sup>90</sup>, i. e. water vapour and dust.

The mechanism for the downward mixing of stratospheric air thus must be such as to treat water vapour carrying HTO (water in the stratosphere most probably is mainly vapour), and the fine particulate matter carrying Sr<sup>90</sup> in essentially the same way. This result is not unexpected, and it appears that all present theories of the fallout mechanism (STEWART, N. G., OSMUND, R. G. D., CROOKS, R. N. and FISHER, E. N., 1957; MACHTA, L., 1959; LIBBY and PALMER, 1960; FEELY and SPAR, 1961) have this feature implicitly contained. The physical basis is that no appreciable settling of the fine particulates involved in stratospheric fallout occurs so that for all intents and purposes they move with the air mass just as the true gases do. Thus, the expectation would be that all radioactive products of nuclear explosions should show the same fractional rate of downward transport from the stratosphere, and except for the complication of re-entry into the stratosphere for the long-lived gaseous products which have no appreciable surface hold-up, there would be essentially no distinction between any of them, either.

GENERAL DEPENDENCE OF TRITIUM LEVELS ON TOTAL THERMONUCLEAR ENERGY RELEASE  
LARGE SCALE UPWELLING ALONG THE CALIFORNIA COAST (Samples from K. O. Emery and H. E. Suess)

The Pacific Ocean surface waters:

	Sample Date	T. U.
Santa Monica Beach	9 Mar. 1960	14 ± 2.3
Johnston Island	30 Apr. 1960	21 ± 2
Samoa, Lago Lago	1 Feb. 1960	6 + 1

show that, in general, the surface waters are much more active than they were before bomb testing started. (1 T. U. in 1952-53 and about 3 T. U. in late 1954 and 1955 after "Castle's" early fallout; Begemann and Libby, 1957; Gilletti, Bazan and Kulp, 1958.)

In fact, using the experience on the North American continent, where the diluting effects of very low T concentration water is very much smaller than in the open ocean, we can see in Fig. 2 that the rise in T content in post-early-fallout surface waters or land rains (three to six months after the tests) is proportional roughly to the estimated total number of megatons of ordinary explosive energy equivalent of thermonuclear fusion energy released (Libby, 1959) despite the wide range of firing conditions with consequent wide variations in local and quick fallout of tritium into the ocean in the case of some of the tests in the Pacific. Therefore, we can expect

that the surface waters of the oceans in general must rise in the manner indicated in Fig. 2 and that the average for the northern oceans now should be about 8 T. U.

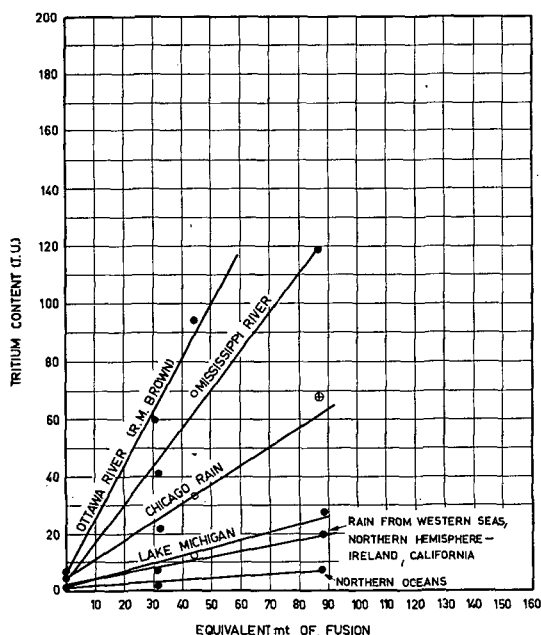


Fig. 2

Bomb Tritium Plot.

O Data of Begemann (unpublished)

X Data of Barrett (unpublished)

(Values are for post fallout; Aug. 1955; Sept. 1956; Aug. 1959)

Consequently, it is with extreme interest that we observe values of 2 T. U. or less in surface ocean water.

TABLE III  
PACIFIC (SOUTH OF SANTA CRUZ ISLAND OFF CALIFORNIA COAST) SAMPLES  
FROM K. O. EMERY, U. S. C.

		T. U.
Lat. N. 32°50.2'	Long. W. 119°42.2'	1.8 ± .3
		0.55 ± .4
Lat. N. 31°52'	Long. W. 120°26'	1.6 ± .2
		0.9 ± .2

From these data it appears to be very probable that these two points over 75 miles apart, about 100 miles off the lower California coast, are in a large upwelling area such that the water is very largely from the depths with only a small component of recent surface water. Further measurements must be undertaken to elucidate the extent of this area. Professor Emery submitted these samples for the reason that he expected the first to show upwelling. The second was collected as a control point, but it, too, apparently lies within the area.

CONTINENTAL WATER BALANCE AND TURNOVER TIME FOR CONTINENTAL GROUND WATER (Samples from A. C. Wahl and A. F. Hakanson and unpublished Chicago rain data of Begemann and of Barrett)

From Fig. 2 we see that the Mississippi and ground water in the Mississippi Valley in the fall of 1959 after the tritium peak was over registered 119 T. U. as compared to 68 in 1957, and Lake Michigan showed 28 T. U. on February 1, 1960, a rise from about 12 T. U.

TABLE IV  
MISSISSIPPI, LAKE MICHIGAN, AND CHICAGO RAIN LEVELS  
Immediately after the fallout from thermonuclear tests (T. U.)

	Mississippi	Lake Michigan	Chicago Rain
Cosmic Ray (? Mt from Ivy)	4	1.6	6
Post Castle (30 Mt Total Fusion)	43	7	22
Post Redwing (44 Mt Total Fusion)	68	12	33
Post Hardtack & Russian Oct. (87 Mt Total Fusion)	119	28	67

The important question of the turnover time for the ground water in the Mississippi Valley was investigated following the "Castle" T fallout (Von Buttlar and Libby, 1955; Begemann and Libby, 1957). The Mississippi was measured at Rock Island and the results in Table V obtained.

TABLE V  
MISSISSIPPI RIVER AFTER „CASTLE”

Sample Date	T. U.
Jan. 3, 1955	55 $\pm$ 1
Feb. 3, 1955	44 $\pm$ 2
Mar. 1, 1955	40 $\pm$ 2
Apr. 1, 1955	43 $\pm$ 3
May 4, 1955	44 $\pm$ 1
June 2, 1955	42 $\pm$ 1
Aug. 1, 1955	44 $\pm$ 5
Sept. 3, 1955	41 $\pm$ 2

These data strongly indicate that the replacement time for Mississippi Valley ground water is longer than a few months and it was concluded (Begemann and Libby, 1957) that the mean lifetime was about ten years. Shortly after the last of the measurements listed in Table V, further Russian nuclear tests occurred, followed by the Pacific "Redwing" series in 1956 so the curve could not be followed further. At the present time, over two years having elapsed since the last substantial atmospheric injections, the Mississippi is showing 119 T. U. — a value on the curve (Fig. 2) for tritium concentration without turnover — again indicates a long time for turnover.

The hydrology of Lake Michigan is such (Kaufmann and Libby, 1954) (95 m depth



plus a drainage area twice the lake area, with a 50% run off figure) that the observed increase from 12 to 28 T. U. corresponds to  $\left(16 \times \frac{95}{2} \times \frac{10^2}{9}\right) \times \left(6 \times 10^{23} \times 10^{-18}\right)$  or  $500 \times 10^7$  T atoms/cm<sup>2</sup>. This can be compared with the Bedford peak (Fig. 1) of about  $38 \times 10^7$  T atoms/cm<sup>2</sup> (calculated assuming a mean annual rainfall of 0.77 m/yr. and a question is raised by this disparity).

It seems likely that the explanation is that a considerable part of the Bedford rain was low activity Atlantic Ocean moisture, which diluted and reduced the activity levels. However, the Lake Michigan figure ought to be reduced by a factor of perhaps 2 to 3 for re-evaporation; i. e. the Lake Michigan value would be about 9 to 14 if it were not that about half of its tritium had been rained out before and re-evaporated before falling into the lake or onto its watershed. This plus the diluting effect of Atlantic Ocean moisture can explain the apparent discrepancy.

This re-evaporation correction affects the earlier comparison (Begemann and Libby, 1957) between the rise in the surface ocean level due to "Castle" and that observed in Lake Michigan (2 T. U. vs 5.6 T. U.). Taking the Lake Michigan hydrology with an average effective depth of  $\frac{95}{2}$  meters (reduced from 95 m due to drainage from the watershed) and applying a factor of 2.5 for re-evaporation, we estimate that the Lake Michigan increase of 28—1.6 T. U. due to bomb tests should correspond to the observed rise of the average surface northern ocean concentration of 8—0.5 T. U. if the ratio of the effective depth of Lake Michigan  $\frac{95}{2}$  m to the mean mixing depth of the ocean surface water were to be  $\frac{7.5 \times 2.5}{26.4}$ . Thus, we calculate that the average mean mixing depth of the northern ocean surface water is 68 m, a value close to the usually accepted (REVELLE and SUESS, 1957; CRAIG, 1957) mean depth of the thermocline of 75 m.

The new data do not seem to require any substantial change in the mean residence time of ten years for Mississippi Valley ground water. It will be very interesting and important to observe the turnover directly as the years pass.

PAST, PRESENT, AND FUTURE RAIN AND OCEAN TRITIUM LEVELS; TOTAL DEPOSITION AND STRATOSPHERIC RESERVOIR (Samples from J. Byrne, Charles Green, John Harley, M. R. Huberty, John C. Manning, E. A. Martell, Terrill L. Noffsinger, Bruce Taylor, V. L. Van der Hoof)

For the rains of the 1959—1960 period all, of course, are post-thermonuclear and reflect only the effects of stratospheric fallout and re-evaporation. Thus, during the spring and early summer of 1959 the northern hemisphere showed the peaks due to the rapid polar stratospheric fallout from the Russian October 1958 tests (Section IIA and Fig. 1) plus the longer termed stratospheric fallout from the "Hardtack" and earlier Pacific tests which should presumably, on the basis of Sr<sup>90</sup> experience, be reflected in the northern hemisphere by the rain tritium fallout before and after the Russian October tests peak and in the southern hemisphere by the rain tritium fallout throughout this period. The re-evaporation tritium must be taken from the level of the surface waters of both ocean and land corrected for the lower tritium water effective vapour pressure of about 0.95 of that for ordinary water (BOLIN, 1958; PRICE, 1958; AVINUR and NIR, 1960; SEPAL and MASON, 1960; BOROWITZ, 1961).

Taking the southern hemisphere first, we note that the southern hemisphere rains, shown in Fig. 3, seem to show an upward trend from about 5 T. U. at the beginning of 1958 to perhaps 10 T. U. in the first quarter of 1960. There are large individual

variations and the hemisphere-wide average (taken simply by using individual rain-fall samples at one tenth of the weight used for monthly averages) exhibits something like a peak in 1959 following the 1958 tests. This total rise of 5 T.U. might be expected on the basis of the  $\text{Sr}^{90}$  parallelism to amount to an expected rise in the Northern hemisphere over and above the Russian October tests fallout which did not reach south of the equator by something between 5 and 10 T.U., so that taking the early 1958 fallout in the northern hemisphere as a base, we add a calculated 3 T.U. rise due to the effect of the Russian October tests fallout from the 1958 tests on the

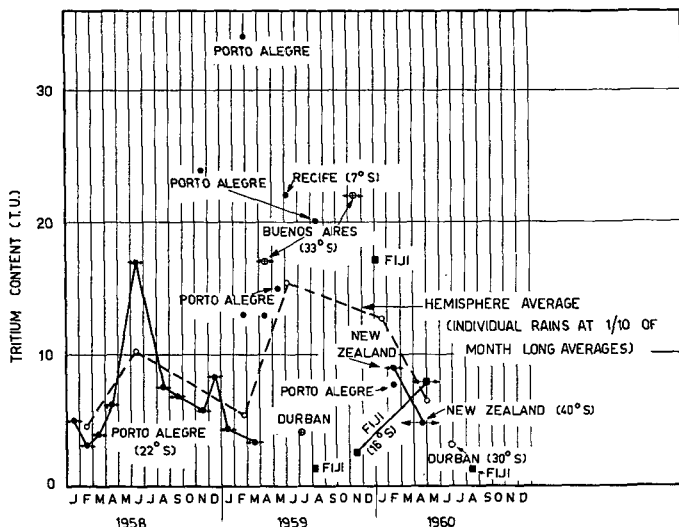


Fig. 3

Southern hemisphere rains.

average northern surface ocean tritium concentration and therefore on the rain. To this must be added the 5 to 10 T.U. of long-term stratospheric drip from the Pacific shots to get a total increase of 8 to 13 T.U. above the early 1958 level of about 8 T.U. for rain received directly from the oceans on the western coasts of California and western Europe. The resultant expected total of 16 to 21 T.U. (Fig. 2) agrees well with the observations in California and western Ireland (Valentia Observatory) as shown in Fig. 4. Thus, we expect that western coasts in the northern hemisphere would have shown an average of about 20 T.U. in the rain during the first part of 1960 and that the southern hemisphere would have had rain tritium levels of about half this or 8 to 10 T.U. in 1960, as was the case.

From these comparisons of the level of fresh ocean rains on the western coastlines it would seem that an 8 T.U. average ocean surface level for the northern hemisphere giving 16 to 21 T.U. for the California and Irish coast rain would correspond to about 3.5 to 4 T.U. for the mean average ocean surface level in the southern hemisphere corresponding to about 7 T.U. being added by stratospheric fallout of presumably Pacific plus Johnston Island thermonuclear explosions with an average stratospheric residence time of about five years (Libby, 1959; Libby and Palmer, 1960). At this rate of fallout for an average annual rainfall of 0.77 m, the amount of T still in the stratosphere is calculated to be

$$5 \times \frac{0.77 \times 7 \times 10^3}{9} \times 6 \times 10^{23} \times 10^{-18}$$

or  $18 \times 10^7$  T atoms/cm<sup>2</sup>. Similarly, the total deposition to date (neglecting radioactive decay and mixing of the surface ocean waters to the great depths) corresponds to

$$\frac{(3.5 - 1) + (8 - 1)}{2} \times \frac{75 \times 10^2}{9} \times 6 \times 10^{22} \times 10^{-18}$$

or  $238 \times 10^7$  T atoms/cm<sup>2</sup> or a total of  $256 \times 10^7$  T atoms/cm<sup>2</sup>. This is equivalent in fusion energy at the rate of 17.5 million eV ( $1.6 \times 10^{-8}$  ergs)/T to 9.3 Mt of fusion. Considering the uncertainty in the fraction of tritium thrown out of a

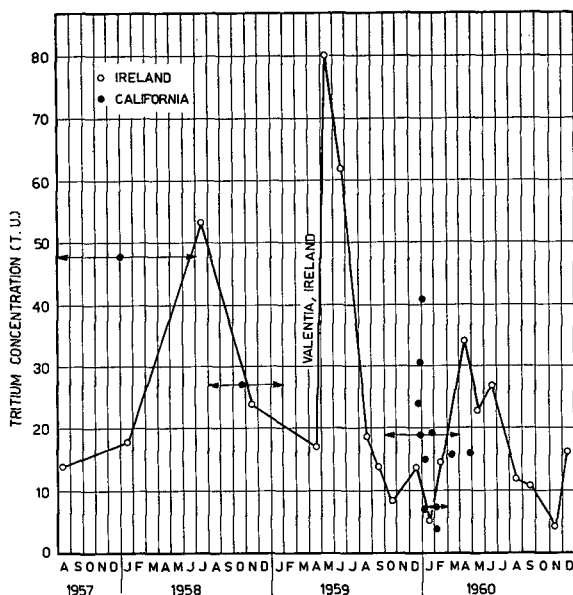


Fig. 4  
Northern Ocean rains; California and Ireland.

thermonuclear explosion as compared to that burned and realizing that perhaps half of the tritium generated falls out locally, we see that this figure is reasonable as compared to the 87 Mt estimated total of fusion energy release.

#### OCEAN MIXING (Samples from K. O. Emery and Giuseppina Aliverti)

Three sets of vertical profile samples — one from the Dead Sea and the other two from two places in the Mediterranean — were run. The one from the Dead Sea seems to show very incomplete mixing below about 35 m, although the deepest sample seems to show some. The two Mediterranean sets — one near Sicily and the other in the Tyrrhenian Sea — both seem to show very definite stratification as between the surface and 150 m. From the differences in concentration, it would seem to follow that the surface waters have not mixed to 150 m in at least six years

HYDROLOGY (Samples from O. R. Angelillo, D. J. Finlayson, Charles Green, M. R. Huberty, John C. Manning, Terrill Noffsinger, H. E. Pearson, A. L. Sonderegger, Bruce Taylor, Robert Thomas, D. B. Willits)

Several hydrological problems in the Southern California area were attempted to test the method.

### *Sparkletts Wells*

An area in Eagle Rock near the Southern California coast has artesian wells (the water is sold for drinking purposes by the Sparkletts Company). The wells are located either along a fault (Raymond Fault) or upstream in a gently sloping aquifer which is exposed to the surface some two miles away. The depth of the aquifer at the fault is about 100 ft, and the general thickness of the aquifer lying between its enclosing clay layers is about 20 ft. The wells along the fault (3987 A, 3987 B, and 3987 F) are in a line 500 ft long and about 250 ft apart. The first two showed essentially no tritium ( $0 \pm 0.26$ ,  $0 \pm 1.5$ ,  $-0.6 \pm 0.6$  for 3987 A, and  $-0.17 \pm 0.5$  for 3987 B), while the third in line showed some ( $4.7 \pm 0.5$  and  $3.5 \pm 0.6$  for 3987 F). One well 3000 ft up-slope in the aquifer (3986 B) showed tritium. Two conclusions appear to be that all of this water is at least several years old or is a mixture of a relatively small fraction of new rain with water old enough to be free of tritium (50 years or so) and that some of the water along the fault and in the aquifer seems to be different. The water from the first two wells right on the fault (A and B) appears to be older, or to have less recent rain mixed in it, while in the third well (F) and in the aquifer look similar with a calculated mean age of only six years or so.

### *San Fernando City Well*

In the City of San Fernando, California, since 1885, a well has been in intermittent daily use. It is 12 in in diameter and 56 ft deep. The general location was in use as a source of spring water for many years prior to 1885 by mission settlers and Indians. Old records and maps show springs and artesian wells at the same place. It is 1.5 miles east of the large San Fernando Reservoir which is filled with Owens Valley rain ( $36 \pm 5$  T. U.). This well water is essentially tritium-free ( $-0.25 \pm 0.3$  T. U.). It thus appears that the well water is dissociated from the surface water system and, in particular, that the reservoir water is not contributing to the well water flow.

The mission well about halfway closer to the reservoir from the city well shows a little rain ( $3.4 \pm 0.5$  T. U.) but is still not part of the reservoir water system.

### *Orange Country Recharge*

The water table near the city of Santa Ana has been depleted by use over the years so a recharge operation has been conducted with Colorado River water (estimated 50 T. U.) and a study of the recharge area has shown a spot-wise distribution of this recharge water. It seems as though the Colorado water goes into certain depleted areas and compresses and raises the level of the old ground water still left into others.

### *Catalina Island*

The single sample analyzed came from one of the important wells (Riess at Avalon) on Catalina Island and was taken with the well casing reaching to 421 ft below sea level. The total depth of the well was 987 ft with a clear depth of 922 ft, and the bottom of the casing was 856 ft below the surface. The result,  $2.5 \pm 0.8$  T. U., shows that the water is old — at least of pre-bomb age — or is a dilute solution of recent rain with tritium-free water from some old source.

## MONTEBELLO FOREBAY

The seven-year-old recharge operation with Colorado River water in the Montebello Forebay of the central basin of the Los Angeles County Flood Control District seems not to have reached the wells sampled to any appreciable extent and all three aquifers, the one below the Silverado at Rio Hondo (sample 1600 Z), the upper Silverado (sample 1599 D), and the Gaspar (sample 1519 T) consist of water ten years old or older.

## MOLOKAI DIKE COMPLEX

The vertically-stratified rocks in the old volcanic crater on the Island of Molokai, Hawaii, are shown to have water of an age of several years stored in them. This is of considerable importance to the Hawaii Water Authority in assuring a steady supply on the downwind (lee) side of the island mountain by a tunnel cutting through to a stream on the wet upwind (windward) side. The permeable compartment banded by volcanic debris can be used for water storage.

## Conclusions

The tritium water method seems to have promise of general geophysical use, particularly in meteorology, oceanography, and hydrology. An urgent need for making water collections for the checking of questions arising in the future exists at the present. In particular, a carefully planned collection of continental rain, river, and lake waters and a wide-scale sampling of surface ocean waters should be made in order to follow the movements of the bomb tritium.

## ACKNOWLEDGEMENTS

The author is very grateful to Bruce Taylor and Martin Hackendorf for the supervision of the tritium measurements for several months and is especially grateful to Joel Leventhal, Dan Benor, Arthur Gittleman, Gerry Marvray, and other undergraduate students for part-time assistance in making the measurements.

Finally, it is particularly pleasant to thank the sources of financial support — the Water Resources Center of the University of California, the late Martin Huberty, Director; the University Research Committee and the United States Air Force Office of Scientific Research.

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**CALIFORNIA AND HAWAII****PART A: RAIN LEVELS***Los Angeles rain*

Individual rains collected by W. F. Libby at 1016 Chantilly Road, Bel Air.

Comment: These values certainly agree with other U.S. west coast rains for this period (cf. Adam Well, Santa Maria River recharge stage of winter 1959–1960).

Dec. 20, 1959	$24 \pm 1.0$ T.U.
Dec. 24, 1959	$30 \pm 6$ T.U.
Jan. 9, 1960	$41 \pm 5$ T.U.
Apr. 27, 1960	$16 \pm 1$ T.U.

*U.C.L.A. Campus*

Jan. 26–27, 1961	$14 \pm 0.7$ T.U.
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*Canyon View Drive, Brentwood*

Collected by Anneliese Haber.

Jan. 26–27, 1961	$19 \pm 1.6$ T.U.
Mar. 15, 1961	$16 \pm 0.6$ T.U.

*San Gabriel dam*

Rainfall collected in the reservoir behind the dam from the canyon watershed. Collected and submitted by the Los Angeles County Flood Control District, Charles Green of the Foundation and Testing Division.

Comment: The rainfall level for the winter season of 1957–1958 is reasonable considering the sizeable hydrogen bomb tests conducted by the USSR in Aug., Sept., and Oct. of 1957 and again in Feb. of 1958. The values for the winter of 1958–1959 are perhaps low compared to those observed in Bedford, Massachusetts, and are more in line with those found in Valentia, Ireland, also exposed to the open sea.

Mar. 1–May 1, 1958	$48 \pm 2.2$ T.U.
Jan. 5–Apr. 26, 1959	$16 \pm 1.3$ T.U.

*Salinas River water*

Collected Nov. 29, 1959, and submitted by Bruce Taylor.

Comment: These values are lower than for pure rain as shown in Lake Nacimiento (21) and Jolon Rain (27). Apparently some old ground water is involved in the river flow.

At King City, Nov. 29, 1959	$8.3 \pm 0.5$ T.U.
At Bradley, Nov. 27, 1960	$12 \pm 0.4$ T.U.
At mouth where salt was 1.8% vs. 3.4% for sea water	$1.1 \pm 0.5$ T.U.

*Orange County rain*

Rain collected in Orange County, at County Building on Dec. 24, 1959. Collected and submitted by M. R. Huberty, Water Resources Center, U.C.L.A.

$19 \pm 2$  T.U.

*San Dimas rain, snow and hail*

Rain, snow, and hail collected by R. A. Merriam, San Dimas Experimental Forest, in East Los Angeles. Submitted by M. R. Huberty, Water Resources Center, U.C.L.A.

Dec. 24, 1959	$7.5 \pm 0.6$ T.U.
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*Monroe Canyon gaging station*

Rain collected and submitted by M. R. Huberty.

*Westwood Los Angeles water*

Samples taken from the tap on the University of California at Los Angeles campus in Westwood.

Comment: This water is thought to be from the Owens Valley reservoir as of about six months earlier according to Bill Ree of the Los Angeles Department of Water and Power and Dr. Pearson of the Metropolitan Water District of Southern California.

*Santa Barbara rain*

Collected at the Hope Ranch in Santa Barbara by Dr. V. L. Van der Hoof and submitted by him.

*Jolon rain*

Rain collected five miles from Jolon, California, neighbouring the Hunter Liggett Military Reservation on the road to King City. Collected by W. F. Libby.

Comment: This is very low. It appears as though this rain must have been from an upwelling area in the ocean (cf. Section on Sea Water), and have had little time aloft.

*Lake Nacimiento water*

This water was rain collected mainly during the preceding winter with perhaps some hold over from the rain of the preceding year. Collected and submitted by Bruce Taylor.

Comment: The value appears to be a little lower than the average for California rain for these periods. Perhaps some old ground water is involved in the run-off.

*Hawaii surface water*

Surface water from the Island of Molokai. Collected and submitted by Terrell L. Noffsinger, of the Land Study Bureau, University of Hawaii.

Comment: It appears that the stream sampled on Molokai is low as compared to the general average for the Pacific, which probably is around 10 to 15 T.U., so it may contain some old ground water or be due to upwelling in the Pacific Ocean upwind as in the case of the Jolon rain.

## PART B: HYDROLOGICAL APPLICATIONS

## CATALINA

*Catalina Island well:* Water from Avalon Public Service Well No. 1 (Riess) located at Avalon, Catalina Island, California. Surface elevation of top of well 435 ft above sea level. Depth of well 987 ft. Clear depth of well 922 ft. Bottom of  $8\frac{1}{4}$  in casing, 856 ft depth or 421 ft below sea level. Sample taken on Mar. 30, 1960. Collected and submitted by O. R. Angelillo, Los Angeles, and the Avalon Public Service Co., W. L. Scott, President.

Comment: This well water is old. Certainly older than 1954 when the first rise in rain tritium levels due to hydrogen bomb testing occurred.

## SPARKLETTS WELLS

*Sparkletts Well:* Water from Well No. 1 (Los Angeles Water District No. 3987 A) at the Sparkletts Drinking Water Corporation plant at 4500 York Boulevard in Los Angeles. The well is about 100 ft deep. The well is perforated all the way with a gravel envelope. The water comes from a layer covered with a hard layer of blue-black clay. Sample taken Apr. 11, 1960. Submitted by O. R. Angelillo, Los Angeles.

Dec. 3, 1959

$9.1 \pm 1.7$  T.U.

Jan. 10 - Feb. 28, 1960

$1.5 \pm 0.6$  T.U.

Mar. 12, 1960

$21 \pm 2$  T.U.

Aug. 16, 1960

$12 \pm 0.8$  T.U.

Jan. 9, 1960

$14 \pm 0.7$  T.U.

Feb. 1, 1960

$3.5 \pm 0.4$  T.U.

Dec. 2, 1960

$6.9 \pm 1.5$  T.U.

Nov. 26, 1960

$2.8 \pm 0.5$  T.U.

Nov. 19, 1959

$21 \pm 1$  T.U.

Nov. 27, 1960

$10 \pm 0.5$  T.U.

Aug. 2, 1960

$3.1 \pm 1.6$  T.U.

$2.5 \pm 0.8$  T.U.

$0 \pm 0.26$  T.U.

$0 \pm 1.5$  T.U.

$0.3 \pm 1.0$  T.U.



Second sample collected under full artesian flow by D. J. Finlayson, of the State Water Rights Board. Submitted by Mr. Finlayson.

Oct. 10, 1960

$- 0.61 \pm 0.6$  T.U.

Comment: This water appears to be at least 40 years old, calculating from the cosmic ray tritium level of 2 to 3 T. U. for rain in California which applied prior to 1954 when hydrogen bomb tritium arrived first in appreciable quantities.

*Eagle Rock area; Sparkletts No. 3:* Water collected on June 24, 1960, from Well No. 3 (Los Angeles Water District No. 3987 F) at the Sparkletts Drinking Water Corporation, at 4500 York Boulevard in Los Angeles. This well is about 500 ft east of No. 1 (Sparkletts Well). It has a total depth of 278 ft and is perforated from 124 to 129 ft, and again from 145 to 151 and from 216 to 266 ft. It lies just upstream from the Raymond Fault. This well and the Sparkletts Well and Eagle Rock area Well No. 3986 B all three lie in a simple artesian pressure area and forebay the lower end of which is defined by the Raymond Fault. From the fault upstream approximately 7500 ft to the north, the formation consists of an aquifer overlain by a relatively impervious aquiclude of sandy clays. In the area over 7500 ft northerly, the aquifer is exposed to form a forebay area. Collected by Brown and Gonzales and submitted by D. J. Finlayson, of the State Water Rights Board.

$4.7 \pm 0.5$  T.U.

Second sample was taken under full artesian flow and submitted by D. J. Finlayson, of the State Water Rights Board.

Oct. 9, 1960

$3.5 \pm 0.6$  T.U.

Comment: This is old water but apparently not as old as that from Sparkletts Well No. 1—500 ft to the west and also lying on the fault. Since rain has been well above 4.7 T. U. in this area since 1954, it appears to be about six years old, or, of course, have a small amount of recent rain in it.

*Eagle Rock area; Sparkletts No. 2:* This well (Los Angeles Water District No. 3987 B) is located between Sparkletts Well No. 1 and No. 3 about equidistant. It is gravel packed from 70 ft to 150 ft below ground level. Sampled on Oct. 9, 1960, while under full artesian flow and submitted by D. J. Finlayson, of the State Water Rights Board.

Oct. 9, 1960

$- 0.17 \pm 0.5$  T.U.  
 $1.0 \pm 0.2$  T.U.

Comment: This water appears to be at least 40 years old, calculated from the cosmic ray tritium level of 2 to 3 T. U. in California, which applied prior to 1954, when hydrogen bomb tritium arrived in appreciable quantities.

*Eagle Rock area Well No. 3986 B:* Water collected on June 24, 1960, from Well No. 3986B, on the Cauchon property at Ridgeview in Eagle Rock. This well was located 3000 ft northerly of the Raymond Fault in the pressure area between the Fault and the surfacing of the aquifer about 4500 ft further north.

$2.1 \pm 0.7$  T.U.

Comment: This also is old water although, again, apparently not as old as the water from Sparkletts Well No. 1. It, too, like Well No. 3, appears to be about six years old.

General Comment: All the water in the aquifer leading to the Raymond Fault is several years old. Some is older as though different rates of recharge in different parts of the aquifer were involved.

## SAN FERNANDO

*San Fernando City Well No. 1:* City Well No. 1 located at the intersection of 4th Street and Hubbard Street in the city of San Fernando. This well is 12 in in diameter and 90 ft deep. It produces 900 gal (U. S.) of water per min and is pumped intermittently into the city reservoir. It has been in use since about 1885. The general location was used many years prior to that time by Mission

$- 0.25 \pm 0.3$  T.U.

settlers and Indians. Old records and maps show springs and artesian wells located at this same location. It is about 1.5 miles E of the lower San Fernando Reservoir. Sample was taken on Sept. 30, 1960, by S. E. Bergman. Submitted by A. L. Sonderegger.

Comment: No recent rain in this water — in particular, no appreciable flow from the lower city of San Fernando Reservoir 1.5 miles to the east.

*Lower city of San Fernando Reservoir*: Collected by S. E. Bergman Sept. 30, 1906. Submitted by A. L. Sonderegger.

$36 \pm 5$  T.U.

Comment: This water is higher than recent rains and would appear to be coming mainly from the Owens Valley through the aqueduct.

*Mission Well No. 5*: Located about halfway between the Reservoir and City Well No. 1.

$3.4 \pm 0.5$  T.U.

Comment: This water is not reservoir water.

### KERN RIVER

*Kern River*: Sample taken from the Kern River near Bakersfield, California, on the Rio Bravo Ranch about  $\frac{3}{4}$  mile west of junction of Cottonwood Creek with the river, on Apr. 6, 1960. The Kern River is thought to be the ultimate source of most of the ground water in the area sampled by the Standard Oil Well, Amerada Well, and Haddad Well, although some water no doubt flows in from Cottonwood Creek. Sample collected and submitted by John C. Manning, Bakersfield..

$16 \pm 0.6$  T.U.

Comment: This result indicates that the Kern River at this point has some old water, since the expected value for new rain or snow would exceed 20 T. U.

*Standard Oil Well*: Sampled Apr. 6, 1960, at point 2 miles due south of sampling point of Kern River sample. The well is thought to be producing from both the upper Kern River formation water sands and from the lower Santa Margarita water sands. Some oil is present from oil streaks in the upper formation. There is thought to be no recharge from surface rain. Sample collected and submitted by John C. Manning, Bakersfield.

$5.7 \pm 0.6$  T.U.

Comment: This result taken with the Kern River value of  $16 \pm 0.6$  T. U. is compatible with the proposed hydrological flow pattern, assuming the water from the Santa Margarita sands to be too old to contain tritium.

*Haddad Well*: Water collected on Apr. 8, 1960, from the Haddad Brothers Well about five miles south of the Kern River and about two miles southeast of the Standard Oil Well. Thought to be downstream for underground flow from the Cottonwood Creek about  $2\frac{1}{2}$  miles northeast. Collected and submitted by John C. Manning, Bakersfield.

$21 \pm 1.4$  T.U.

Comment: This is young water and the well is subject to rapid recharge with rain not over one or two years old.

*Amerada Well*: Water collected on Apr. 8, 1960, from Amerada Well about two miles from the Kern River on the Rio Bravo Ranch. Thought to be downstream for ground water flow from the Kern River. Collected and submitted by John C. Manning, Bakersfield.

$31 \pm 5$  T.U.

Comment: This well is subject to fast recharge. The water is very young, perhaps six months or one year old.

### SALINAS VALLEY

*Salinas Valley and associated wells*: The King City Municipal Well, Canal St. 2 is near the Salinas River, into which the Nacimiento Lake water is discharged. The Hickey well is about one

King City Municipal Well on Nov. 29, 1959

$2.0 \pm 0.3$  T.U.

mile from the Salinas River and in Pine Canyon, which opens onto the Salinas Valley. The Jolon Well is across the Jolon Grade from the Salinas Valley. Samples collected by Bruce Taylor and W. F. Libby.

Comment: All these wells seem to be old water, at least 6 years old in King City, and possibly 40 years old in the Hickey Well in Pine Canyon and the Jolon Well.

J. C. Hickey Well, Pine Canyon, on Nov. 29, 1959  
 $0.6 \pm 0.3$  T.U.

Jolon Well, on Feb. 21, 1960  
 $0.3 \pm 1.8$  T.U.

### SAN BERNARDINO

*San Bernardino County well*: Well water from 829-ft well perforated in bottom 500 ft, located 3 miles east of Yucaipa in San Bernardino County (location Sec33EZ, T1SR1W, 1090 ft east of west line of Section 33, and 1410 ft north of south line of Section 33). Sample taken on Mar. 25, 1960, by Mr. Chandler of the San Bernardino Municipal Water District. Submitted by D. B. Willits and Robert Thomas of the Southern California District of the State Department of Water Resources.

Comment: This water is not recent rain.

$7 \pm 2$  T.U.

### ORANGE COUNTY RECHARGE

*Orange County Wells*: Orange County, in common with many areas in Southern California, is experiencing an overdraft on its ground water basins. To augment the natural recharge of the Santa Ana basin water from the Metropolitan Water District (Colorado River) is used for recharge. Four samples were collected during Mar. 1960 from the Lower Santa Ana Basin to check the recharge effect. Submitted by M. R. Huberty, Water Resources Center, U. C. L. A.

*River Trout Farm (74-18-5B)*: This is a surface water sample from the upper part of the alluvial fan at SE $^{1/4}$  of SW $^{1/4}$  of Sec 7 T4 SR9N.

Comment: This is not recent rain water.

Mar. 21, 1960  
 $2.2 \pm 0.9$  T.U.

*Orange Co. Well No. 3 (91-37-11A)*: Water collected from well located on mid portion of the basin in SW $^{1/4}$  of the SW $^{1/4}$  of Sec 34 T48 SR10W. It is the Orange County District Well No. 3.

Comment: This water is younger than six years. The general level of rain in this area prior to 1954 was about 2 T.U.

Mar. 21, 1960  
 $9 \pm 2.9$  T.U.

*Orange Co. Well (112-10-11A)*: Water collected from the J. E. Lecravian Irrigation well located about 2 $^{1/2}$  miles from the coast near the lower end of the basin in NE $^{1/4}$  of SE $^{1/4}$  of Sec 36 T5SR11W.

Comment: This is old water like the River Trout Farm surface water.

Mar. 22, 1960  
 $2.8 \pm 0.9$  T.U.

*Orange Co. Well (77-13-16A)*: Water collected from the Yerba Linda County Well located near the head of the alluvial fan about one mile from the stream channel of the Santa Ana River.

Comment: This water is younger than six years.

General Comment: It appears that recharge is working and is creating islands of new water in an old water table.

Mar. 22, 1960  
 $8.4 \pm 1.1$  T.U.

### SANTA MARIA VALLEY

*Santa Maria Valley; Adam Well*: Water collected from well (No. 10/33-21R1) on the L. H. Adam property on the flood plain of the Santa Maria River. There was no surface flow at the time. It receives recharge directly from infiltration of river flow during each season of run-off. Collected and submitted by John C. Manning, Bakersfield.

Comment: Looks right for rain and river water in this area.

Apr. 13, 1960  
 $19 \pm 1.2$  T.U.

*Santa Maria Valley: Gilliland Well:* Water collected from the Gilliland well (Old Norsking Well No. 9/33-8 Kl.) on Orcutt upland about 5 miles south and upland from Santa Maria River (T9N-R33W). Bradley Canyon lies between this well and the river. It is thought to receive recharge only from surface infiltration and small ground water flow. Collected and submitted by John C. Manning, Bakersfield. Both this and Adam Well are described thoroughly in USGS Water Supply Paper No. 1000.

Comment: This well is fed mainly by ground recharge of water at least five or six years old on the average.

Apr. 13, 1960

$3.2 \pm 0.8$  T.U.

#### MONTEBELLO FOREBAY

Samples of ground water taken to provide data for the Montebello Forebay of the central basin of the Los Angeles County Flood Control District. Collected and submitted by Charles Green of the L. A. Flood Control District.

*Sample 1600Z:* Taken from well perforated between 525 and 535 ft in the lowermost aquifer of the Rio Hondo Spreading Grounds. This aquifer is thought to be below the Silverado. Water level in the well was 90.81 ft above sea level.

$1.6 \pm 0.7$  T.U.

*Sample 1599D:* Well near Rosecrans Boulevard and the San Gabriel River. perforated between 626 and 628 ft. Water level was 94.9 ft above sea level. Near the top of the Silverado Aquifer.

$1.9 \pm 0.7$  T.U.

*Sample 1519J:* Well near Rosecrans and Atlantic Boulevards perforated between 105 and 127 ft in the Gaspar aquifer. Water level 106.8 ft above sea level. The Gaspar Aquifer is above the Silverado and just below the Los Angeles River.

$1.8 \pm 0.6$  T.U.

$1.8 \pm 0.6$  T.U.

Comment: The area from which the samples were taken was recharged with Colorado River water in the late summer of each year, beginning in 1954. The results show the water to be older than a completely mixed recharge in all three cases and not to contain Colorado water nor recent rain in any appreciable percentage.

#### MOLOKAI

*Molokai Dike complex:* In an attempt to establish approximate length of time water has been stored in an old volcanic eruption with vertical wall components called a dike complex, samples of the dike water in the case of a tunnel on the Island of Molokai have been taken and studied. The five mile long tunnel extends from the dry side of the island to the wet side and is now in the final stages of construction. It will intercept a stream of water on the wet side of the island and carry it through to the dry side and thus furnish ample water during the winter months for irrigation.

During the summer months the stream flow is often inadequate, and the terrain is so rugged that damming of the stream is not practical. However, it is expected that the geological rock formation near the stream will serve as a reservoir; and, in fact, it was thought that once the dike complex was reached by the tunnel, stored water would be released. This proved to be the case. The point of the tritium measurement is to show whether the water from the dike complex is old water or is recent rain which traveled by rapid percolation through the soil. If the water proves to be low in tritium, then the area can be assumed to have characteristics for holding water and can be used as a reservoir to store water during winter for use during the dry summers. In fact, if the dike complex does not hold water for a period of several months, then five or six pumps will have to be installed further down the stream and run more or less continuously during the

summer to lift water approximately 1000 ft to be discharged into the tunnel.

*The first sample* was taken on Jul. 17, 1960, from a horizontal hole core drilled 15 ft left of the tunnel centre line at Station 236 + 08 L.

$0.21 \pm 0.3$  T.U.

*The second sample* was taken Jul. 17, 1960, from springs issuing at the tunnel spring line at Station 247 + 50 L.

$2.8 \pm 0.4$  T.U.

*The third sample* was taken Jun. 18, 1960, from Station 244 + 86. The samples were collected by Robert T. Chuck of the State of Hawaii Water Authority and submitted by Terrell L. Noffsinger, of the Land Study Bureau, University of Hawaii.

$0.38 \pm 0.3$  T.U.

Comment: It appears that the second sample at the tunnel spring may have been five or six years old. It is completely clear, however, that both the first and third samples were older water, much older than 6 years, in view of the bomb test tritium level since 1954. The present Pacific surface water is 10 to 15 T. U.

## RIVERS, LAKES AND RAINS FROM COLORADO, MICHIGAN AND MASSACHUSETTS

### COLORADO RIVER WATER:

Collected February 1960 by Dr. H. E. Pearson of the Metropolitan Water District.

$52 \pm 1.4$  T.U.

### MISSISSIPPI RIVER WATER

Collected Oct. 16, 1960, at St. Louis and submitted by Dr. A. C. Wahl.

$119 \pm 2$  T.U.

Comment: This value, though high, is not as high as expected. Further measurements are indicated.

### LAKE MICHIGAN WATER

Lake Michigan water taken on Feb. 1, 1960, by A. F. Hakanson of the Chemistry Department, University of Chicago.

$28 \pm 3$  T.U.

Comment: This is to be compared with the pre-bomb cosmic ray tritium level of  $1.64 \pm 0.04$  (Kaufman and Libby) and the post-"Castle" 7.5 T. U.

Taking the re-evaporation downwind effect, which probably amounts to about a factor of three as judged from the cosmic ray data, the "Castle" ocean rise should have been  $\frac{5.6}{3}$  to about 3 T. U. from 1, and the present northern ocean level should be about 9 T. U., which appears to be an acceptable value.

### RAINS FROM BEDFORD, MASSACHUSETTS

Rains collected at Bedford, Massachusetts, by E. A. Martell of the United States Air Force Cambridge Research Center. Submitted by E. A. Martell.

Comment: The Bedford tritium fallout curve from the weapons tests in 1958 closely follows that for  $\text{Sr}^{90}$  rising to a peak in April and falling away to the world-wide rate by August or September. The  $\text{Sr}^{90}$  rates (mc /square mile/ in of rain) for the  $30^\circ$ — $50^\circ$  N band were as given below:

Jan. 1959	0.7
Feb. 1959	0.7
Mar. 1959	1.6
Apr. 1959	1.6
May 1959	1.5
June 1959	0.8
July 1959	0.4
Aug. 1959	0.2
Sept. 1959	0.1
Oct. 1959	0.1

## RAINS FROM BEDFORD, MASSACHUSETTS (cont.)

The proportionality constant was about  $1 \text{ mc/Sr}^{90}/\text{mi}/\text{in} = 130 \text{ T. U.}$

Nov. 1958	Nov. 9-16, 1959
65 $\pm$ 11 T.U.	12 $\pm$ 1.0 T.U.
Jan. 1959	Nov. 16-19, 1959
43 $\pm$ 6.6 T.U.	55 $\pm$ 1.4 T.U.
Feb. 1959	Nov. 19-25, 1959
116 $\pm$ 3 T.U.	12 $\pm$ 1.2 T.U.
Mar. 1959	Nov. 25-30, 1959
159 $\pm$ 4 T.U.	31 $\pm$ 3.2 T.U.
Apr. 1, 1959	Nov. 30-Dec. 7, 1959
292 $\pm$ 15 T.U.	12 $\pm$ 1.2 T.U.
Apr. 9-13, 1959	Dec. 21-28, 1959
72 $\pm$ 1.6 T.U.	9.8 $\pm$ 0.7 T.U.
Apr. 13-20, 1959	Dec. 28-29, 1959
220 $\pm$ 2.7 T.U.	42 $\pm$ 1.7 T.U.
May 25-June 3, 1959	Dec. 29, 1959-Jan. 4, 1960
220 $\pm$ 7 T.U.	16 $\pm$ 1.4 T.U.
June 15-June 18, 1959	Feb. 4-8, 1960
174 $\pm$ 2.3 T.U.	15 $\pm$ 0.8 T.U.
June 23-26, 1959	Feb. 8-12, 1960
89 $\pm$ 1.3 T.U.	106 $\pm$ 2.8 T.U.
July 7-July 13, 1959	Feb. 12-15, 1960
74 $\pm$ 7 T.U.	21 $\pm$ 0.8 T.U.
July 14-15, 1959	Feb. 15-19, 1960
168 $\pm$ 4.3 T.U.	14 $\pm$ 0.9 T.U.
July 16-20, 1959	Feb. 24-26, 1960
152 $\pm$ 3.6 T.U.	13 $\pm$ 1.8 T.U.
Aug. 6-10, 1959	Mar. 7, 1960
21 $\pm$ 3 T.U.	30 $\pm$ 0.7 T.U.
Aug. 25-31, 1959	Mar. 18-31, 1960
41 $\pm$ 5.3 T.U.	21 $\pm$ 1.2 T.U.
Sept. 29-Oct. 2, 1959	Apr. 1-6, 1960
59 $\pm$ 1.7 T.U.	11 $\pm$ 2.0 T.U.
Oct. 2-8, 1959	Apr. 20-25, 1960
24 $\pm$ 2.1 T.U.	23 $\pm$ 1 T.U.
Oct. 8-9, 1959	Apr. 28-May 2, 1960
20 $\pm$ 1.2 T.U.	85 $\pm$ 5.5 T.U.
Oct. 23-26, 1959	May 2-10, 1960
9 $\pm$ 1.5 T.U.	11 $\pm$ 1.3 T.U.
Oct. 27-Nov. 2, 1959	May 10-16, 1960
42 $\pm$ 4.2 T.U.	35 $\pm$ 1 T.U.
Nov. 5-9, 1959	May 16-24, 1960
11 $\pm$ 6 T.U.	29 $\pm$ 1.0 T.U.
	May 24-June 6, 1960
	37 $\pm$ 1.4 T.U.
	June 1-6, 1960
	50 $\pm$ 29 T.U.
	June 26-28, 1960
	24 $\pm$ 3.6 T.U.
	June 6-July 5, 1960
	53 $\pm$ 1.7 T.U.

## WINE FROM WESTERN NEW YORK

Wine of 1960 vintage (Dry Niagara) from grapes grown at Naples in western New York state by Widmer's Wine Cellars, Inc. Submitted by William Widmer.

Comment: This looks about right for ground water at this locality in the spring and summer of 1960.

90  $\pm$  2 T.U.

## FOREIGN RAINS

## REÇIFE, BRAZIL RAIN

Individual rain sampled for Health and Safety Laboratory of USAEC, John Harley. Submitted by John Harley.

May 2, 1959

$22 \pm 1$  T.U.

Comment: This is in contrast with the higher values in Bedford, Massachusetts, at the same time showing the Bedford tritium fallout most probably was from the Russian October 1958 test series, which, like the Sr<sup>90</sup>, did not reach the southern hemisphere.

## PORTO ALEGRE, BRAZIL RAIN.

Samples of individual rains collected and combined into monthly totals for the United States Air Force Cambridge Research Center. Collected by Jose Luis Paranhos de Araujo, Sr., I. R. M. Coussirat Araujo, Porto Alegre, Brazil. Submitted by E. A. Martell of United States Air Force Cambridge Research Center, Bedford, Massachusetts.

Comment: This rain may well have contained some early (tropospheric) tritium fallout from the United States Hardtack test series at Eniwetok and Bikini in the Central Pacific.

Jan. 1958	Dec. 1958
$5.0 \pm 0.6$ T.U.	$8.5 \pm 0.3$ T.U.
Feb. 1958	Jan. 1959
$3.2 \pm 0.4$ T.U.	$4.4 \pm 0.4$ T.U.
Feb. 25—Mar. 27, 1958	Feb. 25, 1959
$4.0 \pm 0.3$ T.U.	$13 \pm 0.7$ T.U.
Mar. 29—Apr. 26, 1958	Feb. 26—Mar. 3, 1959
$6.3 \pm 0.7$ T.U.	$34 \pm 1.8$ T.U.
June 1958	Mar. 1959
$17 \pm 0.9$ T.U.	$3.5 \pm 0.2$ T.U.
Aug. 1—Sept. 5, 1958	Apr. 1959
$7.6 \pm 0.7$ T.U.	$13.3$ T.U.
Sept. 6—30, 1958	May 1959
$6.9 \pm 0.5$ T.U.	$15 \pm 1.7$ T.U.
Oct. 25—Dec. 2, 1958	Aug. 1959
$5.8 \pm 0.4$ T.U.	$20 \pm 0.4$ T.U.
Nov. 1958	Feb. 1960
$24 \pm 3$ T.U.	$7.8 \pm 0.9$ T.U.

## BUENOS AIRES, ARGENTINA RAIN.

Rain collected at Buenos Aires for the Health and Safety Laboratory of the USAEC, New York City, John Harley. Submitted by John Harley, New York.

Apr. 1959

$17 \pm 1.3$  T.U.

Nov. 1959

$22 \pm 2.4$  T.U.

Comment: Considering that this site is on the eastern shore and considerable re-evaporation may have been experienced by this rain, the value seems in line with the sea water level in the southern oceans of less than 10 T.U. (Samoa Sea Water and New Zealand, Ohakea and Lanthala Fiji Rain).

## VALENTIA, IRELAND RAIN.

Rain water collected monthly at the Valentia Observatory, Caherciveen, Ireland. Submitted by J. Byrne, Secretary of the National Committee for Geodesy and Geophysics, Dublin.

Comment: These levels look like California rains, although somewhat lower, reflecting the lower tritium level of the Atlantic as compared to the Pacific.

Aug. 1957	Jan. 1960
14 $\pm$ 0.9 T.U.	5.0 $\pm$ 0.7 T.U.
Jan. 1958	Feb. 1960
18 $\pm$ 3 T.U.	15 $\pm$ 1.0 T.U.
July 1958	Apr. 1960
53 $\pm$ 1.5 T.U.	34 $\pm$ 2.1 T.U.
Nov. 1958	May 1960
24 $\pm$ 0.8 T.U.	23 $\pm$ 1.2 T.U.
Apr. 1959	June 1960
17 $\pm$ 1.5 T.U.	27 $\pm$ 1.2 T.U.
May 1959	Aug. 1960
80 $\pm$ 20 T.U.	12 $\pm$ 0.7 T.U.
79 $\pm$ 3 T.U.	Sept. 1960
June 1959	11 $\pm$ 0.8 T.U.
61 $\pm$ 2 T.U.	Oct. 1960
Aug. 1959	5.5 $\pm$ 0.4 T.U.
19 $\pm$ 1.4 T.U.	Nov. 1960
Sept. 1959	4.2 $\pm$ 1.2 T.U.
14 $\pm$ 3 T.U.	Dec. 1960
Nov. 1959	16 $\pm$ 1.3 T.U.
8.1 $\pm$ 1.6 T.U.	
Dec. 1959	
14 $\pm$ 1.3 T.U.	

#### NEW ZEALAND RAIN

Rain collected at the Meteorological Observatory at Ohakea by E. A. Monk, for the Health and Safety Laboratory, USAEC, New York, John Harley. Submitted by John Harley.

Comment: Seems to be low as compared to Fiji on Jan. 1, 1960 at 17

Jan. 28—Mar. 31, 1960  
9.1  $\pm$  1.0 T.U.  
Apr. 1—July 1, 1960  
4.8  $\pm$  0.4 T.U.

#### FIJI RAIN, LANTHALA BAY

Rain samples collected by the Meteorological Office at Lanthala Bay. Submitted by John Harley, Health and Safety Laboratory, USAEC, New York City.

Aug. 6, 1959  
1.5  $\pm$  0.4 T.U.  
Nov. 1959  
2.7  $\pm$  0.7 T.U.  
Jan. 1, 1960  
17  $\pm$  1.9 T.U.  
Apr. and May, 1960  
7.9  $\pm$  0.74 T.U.  
Aug. 11, 1960  
1.1  $\pm$  0.6 T.U.

#### LOURENÇO MARQUES, MOZAMBIQUE RAIN

Rain samples collected for the Health and Safety Laboratory of the USAEC, John Harley. Submitted by John Harley, New York.

Comment: This sample seems to show very little expect cosmic ray tritium.

Sept. 14, 1959  
1.5  $\pm$  0.6 T.U.

#### DURBAN, SOUTH AFRICA RAIN

Rain collected at Durban for the Health and Safety Laboratory of the USAEC, New York City, for John Harley. Submitted by John Harley.

July 3—12, 1959  
4.1  $\pm$  0.3 T.U.  
June 23—24, 1960  
3.2  $\pm$  0.8 T.U.



## SEA WATER

## PART A: PRESENT SURFACE CONCENTRATIONS

*Santa Monica Pacific surface water.*

Beach water collected March 9, 1960, by Gerry Marvray at the beach in Santa Monica, California.

$14 \pm 2.3$  T.U.

Comment: This is to be compared directly with the sample collected at the same spot on Jun. 8, 1953, which gave  $0.54 \pm 0.02$  T. U. [H. VON BUTTLAR and W. F. LIBBY, *J. Inorg. Nucl. Chem.* 1 (1955) 75].

*Atlantic surface water.*

Water collected from the Atlantic City Pier at the end of April 1960. The depth of water was 24 ft. Collected by Peter Simpiano. Submitted by O. R. Angelillo.

$23 \pm 1.3$  T.U.

Comment: This value may reflect the fact that rain from the eastern shore is particularly high in tritium.

*Johnston Island surface sea water.*

Surface sea water collected at Johnston Island in the Central Pacific on Feb. 4, 1960, 3 miles offshore where the water depth was approximately 30 ft. Submitted by H. E. Suess, La Jolla.

$21 \pm 2$  T.U.

Comment: This value is so high that it shows incomplete horizontal mixing in a matter of two years — the time since the last surface hydrogen bombs in the Pacific. These surface shots produce surface water of about 20 000 T. U. over an area of perhaps 1000 square miles (unpublished data of the author's on the Navajo test in 1958). Thus, this level could correspond to an area presently about 1 000 000 square miles, or a good fraction of the Central Pacific. It would be of the greatest interest to trace these tritium islands as they grow and to check the results with the  $\text{Sr}^{90}$  and  $\text{Cs}^{137}$ , which should be high also.

*Fiji surface sea water.*

Taken from the surface of Lanthala Bay on Aug. 11, 1960, by the New Zealand Meteorological service.

$8.6 \pm 1.7$  T.U.

Comment: This is the highest value obtained so far for southern surface Pacific Ocean Water. It may reflect southward movement of local tritium fallout from the bomb tests at Bikini or Eniwetok.

*Samoa surface sea water.*

Surface sea water collected on Feb. 1, 1960, at Lago Lago, American Samoa, at approximately  $1\frac{1}{2}$  miles south of Breakers Point  $1\frac{1}{2}$  miles from shore. The water depth at this point was 300 to 400 ft. There was a light rain falling. Submitted by H. E. Suess, La Jolla.

$5.7 \pm 1.0$  T.U.

$6.4 \pm 2.0$  T.U.

Comment: The South Pacific waters ( $15^\circ$  S) seem to be free of the direct fallout tritium from the surface hydrogen bomb tests at Eniwetok and Bikini ( $11^\circ$  N), in contrast to the North Pacific (cf. Johnston Island surface water on February 4, 1960, which had between 21 and 38 T. U.). This appears to be reasonable in terms of the surface currents being generally toward the northwest from the test area and the general system of clockwise circulation in the northern oceans.

*Upwelling Pacific Ocean surface water.*

Surface water samples collected about Aug. 20, 1960, in the area's most intense upwelling just south of Santa Cruz Island (7120) and from the open sea about 80 miles south (7122). The positions were:

$1.8 \pm 0.3$  T.U.

$0.55 \pm 0.4$  T.U.

$1.6 \pm 0.2$  T.U.

$0.9 \pm 0.2$  T.U.

7120: Lat. 32°50.2' N. Long. 119° 42.2' W.

7122: Lat. 31° 52' N. Long. 120° 26' W.

Collected and submitted by K. O. Emery, of the Department of Geology, University of Southern California.

Comment: It appears that extensive upwelling is occurring in this area because the tritium levels are far below other surface sea waters in the Pacific (10–15 T. U.) and elsewhere in the world (5–10 T. U.). It also appears that even the sample farthest south is showing upwelling. Further testing is strongly indicated.

## PART B: MIXING PROBLEMS

### DEAD SEA.

Water from the surface and various depths of the Dead Sea. Collected about Feb. 1, 1960. Submitted by K. O. Emery, Geology Department, University of Southern California.

Comment: It appears that mixing is retarded at 35 meters and that the 45 m and 200 m waters probably are at least six years old, since they show no artificial tritium from the post-1954 tests. It is odd that the 45 m water looks older than the 200 m water.

Surface	8.5 ± 0.3 T. U.
35 m	5.6 ± 0.8 T. U.
45 m	0.3 ± 0.4 T. U.
200 m	1.8 ± 0.3 T. U.

### MEDITERRANEAN SEA

#### Surface and 150 m water.

Water collected from the Mediterranean Sea near Sicily and Sardinia on Oct. 19, 1959, by Prof. Guiseppina Aliverti, Gabinetto di Meteorologia e Oceanografia, Istituto Universitario Navale, Napoli. Submitted by Prof. Aliverti.

Comment: The Mediterranean is not mixed at 150 m, at least at these two localities. Judging from the tritium content of past rain, the 150 m water is at least six years old and may be twenty or more.

South of Sardinia (39° 09' N, 9° 42' E)	Surface Water	5.5 ± 0.6 T. U.
150 m depth at above site		0.51 ± 0.2 T. U.
Centre of Tyrrhenian Sea (39° 59' N, 12° 36' E)	Surface Water	10.6 ± 1.8 T. U.
150 m depth at above site		0.45 ± 0.45 T. U.
		0.03 ± 0.3 T. U.

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## DISCUSSION I

**B. Grinberg** (France): What techniques were used for measuring the tritium concentrations?

**W. F. Libby:** The technique consists in the enrichment by electrolysis of an alkaline solution. The enrichment parallels that of the deuterium, in such a way that the enrichment factor for tritium and for deuterium remain in a constant ratio. This ratio is about 2:1; in other words, the tritium enrichment factor is about twice the deuterium enrichment factor, relative to protium. Details of one particular technique are given in Prof. Östlund's paper in these proceedings. As shown in another paper, that of Mr. Bainbridge, a solution is electrolyzed from,

say, a volume of one liter and is enriched in several steps until a final volume of perhaps 0.5 cc is obtained. Then two measurements are made on this final concentrate. The deuterium and the tritium concentrations are determined. From the observed deuterium concentration one can calculate the deuterium enrichment. Then, by means of the known ratio between the enrichment factors, the original tritium concentration in the sample can be calculated from the final tritium concentration. To put it differently, about one-half to two-thirds of all of the tritium originally present in a typical case is still present in the final 0.5 cc. Thus, by measuring the tritium concentration in the final concentrate and making corrections for losses due to electrolysis, one can determine the original concentration simply by using the volume ratio. Certain laboratories apply the technique because they have observed that the losses are very reproducible. Others do not even measure the final deuterium concentration. I think it is probably wise to measure it, but perhaps not in every sample. However, that is the general procedure. A single sample requires perhaps a week of work and, under the conditions prevailing in the United States, would cost \$ 100—\$ 200 per measurement.

**J. G. Burr** (United States of America): My question concerns the papers read by Prof. Libby, Mr. Bainbridge and Dr. Gat. I did not note any results which showed a zero tritium content for any sample, even though some of them were taken from substances like old glacial ice, which must have been very ancient indeed. Does the apparent tritium count therefore represent a background count or an experimental error or something else?

**W. F. Libby:** We always have some experimental error, but in my paper you will find examples showing that we do obtain zero levels within the experimental error of measurement. For instance, the samples having to do with the Los Angeles hydrological problem include two such examples. It is remarkable how little difficulty we have with contamination in working with such extremely small amounts of radioactivity.

**D. Sunko** (Yugoslavia): I have two questions for Prof. Libby. First, what was the average enrichment of the deuterium after electrolysis and before the final analysis of the tritium? Second, what was the particular reason for electrolyzing the water samples in alkaline solution instead of, as normal, in acid solution?

**W. F. Libby:** In reply to the first question, at our laboratory we normally electrolyze to a level which enables us to use the falling-drop method in analyzing the water for deuterium, which means to between 0.5% and 5%, or something within that general range. Other laboratories, which use different methods of deuterium analysis such as mass spectrometry or infra-red absorption, can electrolyze to a lesser degree. Correspondingly, they would have to use larger samples for the counting but this is quite feasible, as shown by other papers in this Symposium.

**F. Begemann** (Federal Republic of Germany): As one of Prof. Libby's co-workers, I should point out in connection with his explanation that at Chicago we sometimes used to enrich the samples to such a degree that the deuterium content was actually as high as 90—95%, but then the deuterium was diluted to 3—5% so that we could measure it by the falling-drop method. I mention this lest the mistaken impression be given that the enrichment was always such as to produce final deuterium levels only of 3—5%. As far as sea water is concerned, we of course had levels of up to 90—95% deuterium.

**W. F. Libby:** As to Dr. Sunko's second question, there are two reasons for using an alkaline solution to separate the hydrogen isotopes: first, the electrode reactions

to which it gives rise and, second, the desirability of achieving as large a separation factor as possible. Most of the research on the electrolytic method of separating the hydrogen isotopes was done by people other than those using them for tritium. Few of us in the latter group have done much research on the method itself. The paper we used in our first work with tritium was that of Brown and Daggett in the *Journal of Chemical Physics* in 1934. This paper contains considerable background detail on the electrolytic process.

**E. Eriksson** (International Atomic Energy Agency): I have no question to ask but would merely like to make a few general remarks, among other things, about the interpretation of data. I think it is a matter of general experience in geophysics and geochemistry that it is very difficult, on the basis of a single parameter, to give a complete picture of what goes on in nature. It is necessary to have more than one property, and in the case of tritium and the circulation of water in nature there are certain other factors which can be determined as well and which would certainly aid in the interpretation of the data. One such factor is the stable isotope ratio. We know that it varies latitudinally and that it gives information on the degree of condensation. Another factor is chloride, which is a very good indicator of marine influences on the water, for instance. I believe that account should always be taken of these two factors when precipitation is analyzed for tritium.

Another matter which should be mentioned is standardization of analysis. In this connection, I believe that there is a need for internationally distributed standards. This is a question on which the Agency is at present working. I also believe that everyone working with tritium equipment should be wary of it. After all, this is a rather new technique and it will certainly be improved in the future. One should therefore always be on the watch for new methods and for improvements calculated to eliminate possible errors.

As regards zero water, the Stockholm laboratory under Prof. Östlund has actually found some in a set of some seven ground water samples from the Sabi valley in Southern Rhodesia. The results are interesting: no tritium was found within the experimental error.

One final remark concerns the sea water samples measured by Mr. Bainbridge. In this case too it would be useful to know the temperature and salinity of the samples. This would aid the interpretation and make it possible to decide whether these rather high values for deep water should be expected or not. After all, this latitude in question ( $41^{\circ}$  South) is a rather critical region: considerable converging of sea water and feeding of the intermediate waters occurs there, so that a large amount of vertical mixing is possible. It is not at all representative of the sea surface in general.

**W. F. Libby:** Mr. Eriksson's remarks are most appropriate. It seems to me that, with all new techniques, we must bear in mind the necessity of constantly standardizing and checking to see that the measurements are sound. I believe that from the data being presented in these proceedings it will be possible to work out many such checks, taking due account of any inherent disagreements between them. However, the Agency could perform a very useful service by furnishing standards for calibration. Among the most important of these is the zero water standard. I therefore hope the Agency will carry forward the plans — which I understand it is already working on — to furnish at least that standard. I would re-emphasize the importance of collecting samples now, before it is too late, and urge that you think about measurements that will possibly be wanted in the future, in the realization that water, of all the common commodities of the earth, is the least

treasured in terms of collection and storage. My experience has been that you are never able to get a water sample unless you save it yourself.

**B. Payne** (International Atomic Energy Agency): In co-operation with the World Meteorological Organization, we have already begun sampling from nearly every corner of the globe. We started early in 1961, and samples are now arriving at several laboratories which are co-operating in their measurement both for tritium and for the oxygen-16 — oxygen-18 ratio.

As regards the standards which Prof. Libby mentioned, the principal delay lies in the lack of zero T. U. water. We have been examining water from the geothermal springs in Lardarello, Italy, samples of which have been counted by the Stockholm group. The results show this water to have a tritium concentration greater than zero T. U. In view of this and also the fact that this water, which contains a considerable amount of impurities, is not particularly satisfactory for handling, we are considering the possibility that glacier ice might be more satisfactory in addition to water from the Sabi valley mentioned by Mr. Eriksson.

# LEVELS OF TRITIUM IN A VARIETY OF NEW ZEALAND WATERS AND SOME TENTATIVE CONCLUSIONS FROM THESE RESULTS

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Abstract — Résumé — Аннотация — Resumen

**Levels of tritium in a variety of New Zealand waters and some tentative conclusions from these results.** A wide variety of natural waters was selected for study in the determination of tritium abundance. Results of a series of measurements of tritium from the Akatarawa Stream, near Wellington, from April 1956 to December 1960 are given to show any evidence of bomb tritium in the rains falling on New Zealand. A comparison of these tritium levels with measurements made on tap water at the Institute of Nuclear Sciences was used in an estimate of the storage time of the Hutt Valley Artesian Reservoir. A limited number of results of measurement of tritium in geothermal bore waters, oceanic waters, Wellington rainwater and alpine snows are presented.

**Concentration du tritium dans diverses eaux de Nouvelle-Zélande et conclusions provisoires tirées des résultats obtenus.** Les auteurs ont choisi un grand nombre d'eaux naturelles pour déterminer leur concentration en tritium. Le mémoire contient les résultats de mesures de la teneur isotopique des eaux de l'Akatarawa (près de Wellington), effectuées entre avril 1956 et décembre 1960; ces résultats montrent si les pluies qui tombent sur la Nouvelle-Zélande contiennent du tritium provenant des essais de bombes. Les auteurs les ont comparés aux résultats des mesures faites sur l'eau de ville à l'Institut des sciences nucléaires, pour évaluer le temps d'emmagasiner de l'eau dans le réservoir artésien de la Hutt Valley. Le mémoire contient aussi quelques résultats de mesures de la teneur en tritium des eaux de forages géothermiques, d'eaux de mer, d'eaux de pluie recueillies à Wellington, et de neiges de montagne.

**Уровни трития в различных водах новой зеландии и предварительное заключение по этим результатам.** Большое количество различных проб природных вод было отобрано для изучения с целью определить избыток трития. Серия измерений трития в водах Акатаравы близ Веллингтона с апреля 1956 по декабрь 1960 года показали наличие в дождевых водах, выпадающих в Новой Зеландии, трития, возникшего в результате испытания атомных бомб. Сравнение этого уровня содержания трития с измерениями, произведенными с водопроводной водой в Институте ядерных исследований, было использовано для определения времени хранения воды в артезианском бассейне Хут-Валлей. Будет представлено некоторое число результатов измерений трития в подземных водах, в океане, в дождевых водах Веллингтона и в альпийских снегах.

**Concentraciones de tritio en diferentes aguas de Nueva Zelandia y conclusiones provisionales basadas en los resultados obtenidos.** A fin de determinar su contenido de tritio, se han seleccionado para su estudio aguas naturales de muy diversa índole. Se indica una serie de mediciones de tritio realizadas con muestras tomadas del río Akatarawa, cerca de Wellington, entre abril de 1956 y diciembre de 1960, que demuestran la presencia, en las aguas de lluvia caídas sobre Nueva Zelandia, de tritio procedente de explosiones nucleares. Se ha establecido una comparación entre estos niveles de tritio y las mediciones realizadas en aguas de grifo en el Instituto de Ciencias Nucleares, a fin de calcular el tiempo de permanencia de las aguas en el depósito artesiano del Valle de Hutt. Se expone un número limitado de resultados de las mediciones de tritio en nieves alpinas y en aguas de pozo geotérmicas, aguas oceánicas y aguas de lluvia caídas sobre Wellington.

## 1. Introduction

The tritium concentration results reported in this paper were collected over a period from mid-1956 to the present time. Originally it was decided to collect water samples from a wide variety of sources for the initial analyses. Samples from the more interesting sources would then be analysed in more detail. This programme has been carried out to a limited extent, but in some of the sampling series there are still gaps because samples were not taken or were lost; and, in many cases, samples have yet not been analysed.

## 2. Experimental

The water samples, having volumes of 3 or 15 l, were enriched by electrolysis. Five electrolytic stages were used to reduce the volume to 0.5 ml. The tritium enrichment is calculated from the formulae:

$$\ln Z = \frac{\alpha}{\beta} \ln Y + \left(1 - \frac{\alpha}{\beta}\right) r \ln N,$$

where  $Z$  is the tritium enrichment,  $Y$  the deuterium enrichment,  $N$  the total volume reduction, and  $r$  the ratio of the volume of water electrolyzed to the total volume of water lost from the cell. Factor  $r$  corrects for spray and vapour losses. The deuterium measurements were made on our mass spectrometer.

The enriched samples were converted to hydrogen over zinc at 400°C. The hydrogen was then passed into the counters and mass spectrometer sample bottles. The counting is described in these proceedings, pp. 343–350.

## 3. Accuracy of results

All results are expressed in terms of tritium units (T.U.), one tritium unit being defined as one part of tritium to  $10^{18}$  parts of hydrogen. By repetition of one sample a number of times the overall accuracy has been estimated as  $\pm 18\%$ . This error is largely caused by uncertainties in estimation of the spray and vapour losses from the cells, in other words, uncertainties in the value of  $r$ . The errors introduced in conversion, deuterium analysis and counting amount to less than 5%. All results are expressed in relation to a tritium water sub-standard, supplied by Tracer-Laboratories Inc., United States of America.

## 4. Results

Table I shows the tritium concentration of the Akatarawa Stream, about twenty miles from Wellington. Monthly samples were collected from this stream from mid-1956, but unfortunately no samples were collected between October 1958 and April 1960. Since this stream flows fairly rapidly, it was felt that the tritium content of its waters would show the overall monthly variations but would tend to smooth out the values of individual rains. The results indicate that there has been approximately a twofold increase in the tritium precipitation rate between 1956 and the present time. Since it has been shown by BROWN and GRUMMITT [1] that the washout time for tritium in the troposphere is approximately 35 d, it is reasonable to assume that the increase in the tritium precipitation rate was caused by the accumulation of stratospheric tritium in the southern hemisphere. This accumulation was probably largely due to the testing of fusion weapon devices during 1957–58.



TABLE I

**TRITIUM CONCENTRATION OF AKATARAWA STREAM SAMPLES, 1956-1960, IN TRITIUM UNITS**

	1956	1957	1958	1959	1960
January		5.5	15.8		
February		5.1	8.1		
March		6.9			
April	4.2	5.9	9.9		
May		10.4			11.1
June		3.0	8.1		8.4
July		4.8	7.2		9.8
August		2.5			11.4
September	4.9	3.6	9.9		19.8
October	7.5	9.1			
November	5.3	11.7			
December	4.5	11.0			
Average	5.28	6.62	9.83		10.3

The relatively large results for October 1956 and September 1960 may be due to a sudden leak from the stratosphere during the spring, as there was for nuclear fission product fallout in the northern hemisphere [2]. The monthly precipitation of  $\text{Sr}^{90}$  in Wellington [3] shows peaks for September 1960 and September-October 1959 that are roughly double the average monthly precipitation.

TABLE II

**UNDERGROUND WATERS****A. Hutt Valley Aquifer**

Sample No.	Date of Collection		T. U.
TW 71	22. 7. 59		4.5
TW 72	10. 9. 59		4.7
TW 73	9. 10. 59		5.3
TW 74	9. 11. 59		4.5
TW 85	21. 3. 60		4.0
TW 87	22. 4. 60		5.7
TW 89	20. 5. 60		4.5
TW 90	20. 6. 60		6.2
TW 95	19. 7. 60		6.2
TW 101	20. 9. 60		6.0

**B. Hawkes Bay Aquifer**

TW 11	15. 3. 57	55 foot well at Fernhill	4.1
TW 12	15. 3. 57	72 foot well at Tyford	2.4
TW 13	15. 3. 57	128 foot well at Longlands	0.95
TW 15	15. 3. 57	130 foot well at Clive	1.3
TW 16	15. 3. 57	250 foot well at Napier	0.79
TW 17	15. 3. 57	130 foot well at Mangateretere	1.1
TW 18	15. 3. 57	Well at Pakowai Rd.	1.5

Samples from the Hutt Valley Aquifer (Table II) have been collected since June 1959. It is assumed that the supply to this aquifer has the same specific tritium

activity as does the Akatarawa Stream. On this basis, the mean storage time for this aquifer was calculated to be five years, a figure that is in agreement with hydrological estimates.

The results shown in Table II (B), taken from the Hawkes Bay Aquifer, were all collected from a number of wells on the same day. This artesian system is covered with an impermeable layer, except for a small region of uncapped gravels near Fernhill, which is assumed to be the area in which the water enters the system. The well at Fernhill is quite close to this uncapped area, while the wells at Tyford, Pakowai, Mangateretere and Clive lie roughly in a straight line. Napier and Clive are quite close to the sea coast. It can be seen that the activities diminish as the distance from the source area increases. The activities of 1 T.U. or less would seem to indicate that some of the water is 20 or more years old.

The tritium concentration of Lake Taupo (Table III with the samples from

TABLE III  
TRITIUM CONCENTRATIONS OF GEOTHERMAL WATERS

Sample No.	Collection Date	Details	T. U.
TT 16	3. 12. 56	Lake Taupo	1.95
TT 20	15. 1. 57	Lake Taupo	2.5
TT 30	21. 2. 57	Lake Taupo	2.7
TT 35	20. 3. 57	Lake Taupo	3.3
TT 41	13. 4. 57	Lake Taupo	2.3
TT 53	11. 7. 57	Lake Taupo	4.7
TT 59	4. 10. 57	Lake Taupo	4.5
TT 80	23. 7. 59	Lake Taupo	1.81

#### BORES

TT 2	3. 10. 56	Bore 26	3.6
TT 61	4. 10. 57	Bore 26	2.18
TT 100	13. 3. 60	Bore 26	0.70
TT 34	20. 3. 57	Bore 13	3.20
TT 90	9. 6. 60	Bore 22	0.32
TT 91	9. 6. 60	Bore 39	0.60
TT 103	7. 4. 60	Bore 67	0.23

#### FUMEROLES

TT 22	29. 2. 56	Big Donald (condensate)	0.67
TT 24	29. 2. 56	Schuberts (condensate)	1.05
TT 25	18. 1. 56	Karapiti (condensate)	0.86
TT 101	18. 3. 60	Karapiti (condensate)	0.50
TT 102	18. 6. 60	Fumerole "K. B." (condensate)	0.88

#### MISCELLANEOUS

TT 26	18. 1. 56	Champagne Pool	1.0
TT 32	21. 2. 57	Lake Wairakei	3.5
TT 37	20. 3. 57	Lake Wairakei	2.5
TT 64	6. 12. 58	Anakeri Springs	3.3
TT 65	8. 12. 58	Soda Springs	1.6

geothermal areas) is somewhat lower than that of the Akatawara Stream. Since Taupo is a lake of considerable size and depth, the lower values could be the result of vertical mixing with old water. The fact that samples taken from nearby Lake Wairakei (TT 32 and 37), a small lake, have tritium concentrations of similar order suggests that a lower tritium activity in the rains in this area is a more likely explanation.

The bores quoted are 8-in steam bores drilled in the Wairakei area for the production of electric power. The fumeroles "Big Donald" and "Schuberts" are on White Island in the Bay of Plenty, while the fumeroles "Karapiti" and "K. B." are in the Wairakei area. The later measurements on bores show similar tritium levels to those of the fumeroles. The earlier bore samples show much higher activities. The bore system probably consisted of a much larger fraction of recent ground water during the early stages, but now it seems to consist largely of old ground water or possibly magmatic water. This conclusion is supported by the fact that the ground water level has dropped considerably over the past five years. Since the activities of the bore samples are not much lower than those of the Hawkes Bay underground waters, underground water cannot be ruled out as a source of the geothermal steam.

TABLE IV  
TRITIUM CONCENTRATIONS OF SEA WATER

Sample No.	Date of Collection	Sample Details	T. U.
TW 21	2. 4. 57	Makara (near Wellington)	1.1
TW 31	10. 6. 57	Makara (near Wellington)	1.8
TW 62	30. 11. 58	Antarctic (100 m depth)	1.5
TW 79	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (surface)	1.96
TW 81	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (100 m)	1.5
TW 75	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (200 m)	0.88
TW 82	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (400 m)	0.80
TW 76	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (760 m)	1.1
TW 77	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (1500 m)	0.63
TW 80	26. 9. 59	Lat. 41°5'S, Long. 178°0'E (2160 m)	1.5

The activities of some sea water samples (Table IV) show remarkable uniformity. The variation of activity with depth would indicate a mixing time of about twelve years.

A number of other water samples are shown in Table V.

TABLE V  
TRITIUM CONCENTRATION OF MISCELLANEOUS WATER SAMPLES

Sample No.	Date of Collection	Sample Details	T. U.
TW 68	19. 6. 59	Snow from Tasman Glacier	17.9
TW 69	23. 6. 59	Snow from Tasman Glacier	10.5
TW 70	26. 6. 59	Old Ice from Tasman Glacier	1.2
TC 1	4. 7. 57	Campbell Island Fresh Water	2.5
TC 5	4. 11. 57	Campbell Island Fresh Water	5.6
TC 13	1. 5. 58	Campbell Island Fresh Water	12.2
TC 11	1. 7. 58	Campbell Island Fresh Water	15.8
TC 15	1. 11. 58	Campbell Island Fresh Water	13.8

## 5. Conclusion

The results in this paper were presented at the Symposium to make known the approximate scale of effort we are putting into this project in New Zealand and the type of information we can obtain of the technique of tritium enrichment and measurement which can be satisfactorily developed. Our preliminary results show:

- (1) That an enrichment of tritium has taken place in the waters of the southern hemisphere. Presumably tritium from H-bomb testing is reaching New Zealand from the stratosphere.
- (2) From results for the Akatarawa Stream, the Hutt Valley Aquifer and the Hawkes Bay Aquifer, there is sufficient variation in tritium concentration between the source of supply and the place of sampling for reasonable estimates to be made of residence time for water in the reservoirs.
- (3) Tritium detection in geothermal bore waters gives additional support to existing physical and chemical evidence that geothermal steam may consist of up to 80% of heated ground water.
- (4) The significance of the detection of tritium in sea water at depth needs further investigation, particularly as the detection of a zero sea water has not as yet been obtained.

## ACKNOWLEDGEMENTS

The authors wish to thank the New Zealand Geological Survey, the New Zealand Oceanographic Institute and the New Zealand Meteorological Department for collecting many of the samples and also H. A. Polach and J. E. R. Penman of this laboratory for supervising the enrichment, conversion and counting of samples and to Messrs J. R. Hulston, F. Knox and Mrs. A. E. Bainbridge for mass spectrometer measurements.

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## DISCUSSION II

**F. Begemann** (Federal Republic of Germany): Could Mr. Bainbridge indicate what is the lowest tritium level his group has observed in New Zealand?

**A. E. Bainbridge** (New Zealand): We have not found any samples of less than 0.2 T.U.

**D. Lal** (India): In connection with the 1959 measurements of tritium concentrations in sea water reported by Mr. Bainbridge, there seems to be essentially no change in the tritium concentration values with increasing depth. This is rather surprising. I should therefore like to ask Mr. Bainbridge whether this could be due to contamination and whether he thinks the results are significant?

**A. E. Bainbridge**: As I indicated in my paper, we are suspicious of these results because the samples were not collected under ideal conditions and had been stored

for some time. I must also point out that the water was collected at the particular station on the request of the New Zealand Institution of Oceanography, which suspected that some anomaly was present. I do not have the results of the work because the sea water samples are still under study and must be correlated with other data. New Zealand and the station in question are in an area of complex and converging systems and it is therefore possible that the data are correct. However, the contamination is certainly not so high. The water vapour level in the southern hemisphere and in New Zealand is low and it is therefore difficult to understand, in view of the large size (15 l) of the starting samples, how enough water vapour could get into our apparatus to give the order of magnitude of specific activity which we obtained. Thus, it is possible that there is some oceanographic anomaly at this point. Our oceanographic ships do not have the time to study the whole ocean. All they can deal with are the anomalies and what this anomaly is will be known shortly.



# TRITIUM CONTENT OF RAINWATER FROM THE EASTERN MEDITERRANEAN AREA\*

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Abstract — Résumé — Аннотация — Resumen

**Tritium content of rainwater from the eastern Mediterranean area.** About 50 samples of rainwater collected during the years 1958—1960 in Israel and neighbouring countries were assayed for their tritium content by gas counting following electrolytic enrichment. The samples included single showers collected at two stations in Israel and one in Cyprus, as well as composite samples accumulated during each rainy season at a number of sites in Israel, Cyprus, Turkey and Greece. In addition samples of cistern water, representative of rain from the 1956/57 and 1957/58 rainy seasons, were also analyzed.

From the air circulation pattern and the timing of thermonuclear tests relative to the local rainy season it is inferred that little direct tropospheric transport of tritium from the test sites into the area occurs. The measured tritium levels hence are due to tritium leakage from high altitudes into lower air layers. Mean atmospheric residence times are estimated for stratospheric tritium from different sources. There is evidence that tritium is only slowly mixed throughout the stratosphere.

Systematic differences between the tritium levels at various sites are explained in terms of the different rain producing situations. It is shown that the extent of mixing of maritime and continental air masses are of paramount importance for the resulting tritium content of rain and that the dimensions of the Mediterranean sea are small compared to the scale of meteorological phenomena involved.

**Teneur en tritium des eaux de pluie dans la région de la Méditerranée orientale.** La teneur en tritium d'une cinquantaine d'échantillons d'eau de pluie prélevés au cours des années 1958—60 en Israël et dans des pays voisins a été déterminée au moyen de compteurs à gaz, après enrichissement électrolytique. L'analyse a porté sur des échantillons de diverses précipitations, provenant de deux stations israéliennes et d'une station cypriste, ainsi que sur des échantillons d'eaux accumulés pendant chaque saison des pluies dans plusieurs régions d'Israël, de Chypre, de Turquie et de Grèce. En outre, on a analysé des échantillons d'eaux de citerne accumulées pendant la saison des pluies de 1956/57 et 1957/58.

Compte tenu de la date des essais thermonucléaires, des courants atmosphériques et de la saison locale des pluies, on peut conclure qu'il n'y a aucun transport troposphérique direct de tritium provenant de la zone des essais vers la région considérée. Les concentrations de tritium mesurées sont dues au passage de tritium des hautes altitudes dans les couches atmosphériques inférieures. On a évalué la durée moyenne du séjour dans l'atmosphère du tritium stratosphérique provenant de diverses sources. Les constatations faites semblent prouver que le tritium ne se mélange que lentement aux masses d'air de la stratosphère.

Les différences constantes entre les concentrations de tritium à divers endroits sont expliquées en tenant compte des différentes situations qui sont à l'origine des pluies. On montre que le mélange des masses d'air maritimes et continentales a une influence primordiale sur la teneur en tritium des eaux de pluie et que l'étendue de la mer Méditerranée est faible par rapport à l'ampleur des phénomènes météorologiques en jeu.

**Содержание трития в дождевой воде, взятой из восточного района средиземного моря.** В течение 1958—1960 гг. около 50 проб дождевой воды было взято в Израиле и соседних странах и подвергнуто количественному анализу на содержание в них трития с помощью газового счетчика после электролитического обогащения. Сюда входили пробы отдельных ливней, взятые на двух станциях в Израиле

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и одной станции на Кипре, а также пробы воды, собранные в течение каждого сезона дождей в ряде мест в Израиле, на Кипре, Турции и Греции. Кроме того, были также проанализированы пробы воды, взятой из водоемов, которые соответствуют сезонам дождей в 1956/57 и в 1957/58 гг.

На основании схемы циркуляции воздуха и времени проведения испытательных термоядерных взрывов в связи с местным сезоном дождей установлено, что не происходит прямого тропосферного переноса трития из районов испытаний в данный район. Следовательно, измеренные уровни трития вызываются проникновением трития из больших высот в низкие слои воздуха. Определяется среднее время пребывания в атмосфере стратосферного трития из различных источников. Совершенно очевидно, что тритий лишь слегка смешан во всей стратосфере.

Систематические различия в уровнях трития в различных местах объясняются различной ситуацией, вызывающей выпадение дождей. Доказывается, что степень смещения морских и континентальных масс воздуха имеет первостепенное значение для вытекающего из этого содержания трития в дождевой воде и что размеры Средиземного моря малы по сравнению с масштабом соответствующих метеорологических явлений.

**Contenido del tritio en las aguas de lluvia de la zona del Mediterráneo oriental.** Los autores analizaron unas 50 muestras de agua de lluvia recogidas durante los años 1958 a 1960 en Israel y países vecinos a fin de determinar su contenido de tritio por recuento gaseoso precedido de un enriquecimiento electrolítico. Entre las muestras figuraban algunas de precipitaciones aisladas, recogidas en dos estaciones en Israel y una en Chipre, así como agua acumulada durante cada temporada de lluvia en una serie de lugares en Israel, Chipre, Turquía y Grecia. Además se analizaron muestras de aguas de cisterna representativas de las lluvias caídas durante las temporadas 1956—1957 y 1957—1958.

La configuración de las corrientes atmosféricas y la relación cronológica que existe entre los ensayos de armas termonucleares y la temporada local de lluvias indican que no se produce ningún transporte troposférico directo de tritio del lugar de la explosión a la zona estudiada. Por lo tanto, la presencia de tritio en las capas inferiores de la atmósfera se debe a la difusión desde las capas superiores. Los tiempos medios de permanencia atmosférica del tritio han sido calculados para el tritio estratosférico procedente de distintas fuentes. Parece demostrado que el proceso de mezcla del tritio en la estratosfera es lento.

Las diferencias entre las concentraciones de tritio que aparecen sistemáticamente en distintos lugares se explican por las circunstancias variables que determinan la precipitación pluvial. Se demuestra que el grado en que se mezclan las masas de aire marítimo y continental ejerce una influencia decisiva sobre el contenido de tritio de las aguas pluviales, y que las dimensiones del Mar Mediterráneo son pequeñas en comparación con la escala en que suceden los fenómenos meteorológicos que intervienen en dicho proceso.

## Introduction

The usefulness of both cosmic ray and artificially produced tritium as a tracer for the movement of water in nature has long been recognized and becomes ever more apparent. Investigations on the tritium content of rainwater, which were performed recently, have outlined some features of the circulation of tritium in the atmosphere following its injection by thermonuclear explosions [1, 2, 3]. However important details, such as the extent of exchange of atmospheric tritium with water on land and ocean areas as well as the rate of descent into the troposphere of tritiated water from a stratospheric reservoir [4], have remained controversial and await additional measurements for their final solution. The present study, in which precipitation samples from Israel and other eastern Mediterranean countries have been analyzed, may contribute somewhat towards this goal; the distinguishing feature of the area being the presence of a fairly large landlocked sea which acts



as a major water source for local rainfall and a regular seasonal precipitation pattern. The results so far available point out some interesting trends; many more observations are needed to confirm them and enable quantitative deductions to be made.

The rainy season in Israel, generally, lasts from September to May; December, January and February being the wettest months. The appearance of rain at that time is then governed by the southward retreat of the subtropical high pressure belt with the result that the Mediterranean sea becomes a favoured path for eastward moving Atlantic disturbances, accompanied by a large number of frontal passages. Other lands of the eastern Mediterranean also have a predominance of rain in winter.

### Sampling methods

Composite rain samples, representing average values over extended periods, were obtained in two ways:

- Rainwater accumulated during the rainy season in water catchments and cisterns was sampled at the end of the rainy season;
- Daily rain samples, collected in standard rain gauges, were poured into plastic bottles which were subsequently sealed hermetically.

Method (b) reliably produced a true average sample of the season's rain. This method was generally used in the programme. Daily samples from extended periods of time were thus combined except during the 1960/61 season where composite samples of every month were stored separately. Method (a) discriminated against small rainfall amounts, which did not reach the reservoir and against the early rainfall of every season. It was also troubled by possible isotope fractionation by evaporation. Nevertheless samples collected according to this procedure were perhaps more representative of the rainwater input into the water storage systems and hence this method may be favoured where the motivation for the analysis is hydrological research.

In addition to seasonal composite samples the water from single strong showers was collected with the aid of large funnels (400 cm<sup>2</sup> in area) which drain into plastic bottles. For this purpose a single shower was defined as all rain falling during a period of continuous or intermittent rain without breaks in the rainfall of more than

TABLE I  
ANALYSIS OF SAMPLING SITES

Site	Location	Latitude (N)	Longitude (E)	Altitude (m)	Distance from seashore (km)	Mean Annual Rainfall (mm)
Rehovoth	Central Israel	31°55'	34°48'	55	12	544
Lod	Central Israel	31°59'	34°54'	40	16	496
Tirat-Yael	Northern Israel	32°57'	35°26'	800	33	> 900
Beer-Sheva	Negev, Israel	31°15'	34°48'	275	46	200
Nicosia	Cyprus	35°10'	33°21'	165	17	390
Prodhromos	Cyprus	34°57'	32°50'	1380	40	965
Adana	Southern Turkey	37°08'	36°12'	20	20	617
Antalya	Southern Turkey	36°57'	30°41'	43	0.3	1033
Maritsa	Rhodos	36°22'	28°07'	34	4	700
Yraklion	Crete	35°20'	25°11'	47	1.5	510
Athens-Hellinikon	Greek Mainland	37°54'	23°44'	7	0.25	390
Methoni	Greece, Adriatic shore	36°50'	21°43'	34	< 1	~ 1000

six hours duration. This definition seems appropriate in climates where rainfall is mainly due to frontal passages.

Details of the sampling sites are given in Table I.

### Experimental

About one litre of every rainwater sample was pre-enriched by electrolysis in two or three stages. A volume reduction of ten was achieved in each stage on iron and nickel electrodes, using conventional techniques. The tritium in the final water sample (of about 1 ml) was, on the average, enriched 470 fold. The performance of the enrichment process was always checked by mass-spectrometric determination of deuterium which was simultaneously enriched. Some of the water was decomposed on zinc in sealed ampoules at a temperature in excess of 450 °C; the resulting hydrogen gas was then introduced into a 1.2 l gas counter (RC1 type 10801) together with toluene quencher.

The counter was operated in the Geiger region in anticoincidence with a ring of cosmic ray counters. Counter sensitivity was found to be  $0.94 \times 10^{-4}$  cpm/cm Hydrogen  $\times$  T.U. This corresponded in the system to a minimum measurable activity of 1.1 T.U. (as defined by HOURS and KAUFMAN [5] for a coefficient of variation  $C_v = \sigma_s/n_s = 0.1$ , where  $\sigma_s$  was the standard deviation of the sample count rate  $n_s$ ), with a 500 fold pre-enrichment, 30 cm hydrogen gas pressure in the counter and overnight count. The long time stability of the counting system was excellent and reproducibility well within the statistical counting error limit. The reproducibility

TABLE II

#### A. COMPOSITE RAINWATER SAMPLES FROM RAIN CISTERN, RUN-OFF CATCHMENTS AND RESERVOIRS

Sampling Site	Collection Period	Rainfall Amounts (mm)	Sample Description	T. U.*
1956/57 Season Ejn Karem Dam near Jerusalem	Nov. 1956—Apr. 1957 sampled Apr. 14, 1957	650	run-off water trapped by open dam	$50 \pm 20$
Tel-Yeruham Northern Negev	Nov. 1956—Apr. 1957 sampled Apr. 15, 1957	175	run-off water trapped in open reservoir	$110 \pm 30$
Beth-Netofa Northern Israel	Oct. 1956—Apr. 1957 sampled Apr. 20, 1957	560	water catchment	$80 \pm 10$
1957/58 Season Kfar Yanuh Northern Israel	Oct. 1957—Apr. 1958 sampled Aug. 14, 1958	798	cistern water	$70 \pm 10$
Tarshiha Northern Israel	Sept. 1957—May 1958 sampled Aug. 1958	690	run-off water	$65 \pm 20$
1958/59 Season Tarshiha	Sept. 1958—May 1959 sampled Sept. 21, 1959	632	run-off water	$230 \pm 20$

\* Errors quoted in section A are the estimated overall errors (including non-statistical errors) which are large in this section. These samples were processed before the laboratory achieved its final accuracy.

TABLE II  
B. RAINWATER COLLECTION

Sampling Site	Collection Period	Rainfall Amount (mm)	Sample Description	T. U.
<i>1958/59 Season</i>				
Tirat-Yael	Oct. 16—17, 1958	24.5	strong single shower	$88 \pm 0.6$
Tirat-Yael	Dec. 7—8, 1958	64	continuous showers	$125 \pm 1.2$
Rehovoth	Dec. 9, 1958	14	shower	$120 \pm 1$
Rehovoth	Jan. 7—8, 1959	45	continuous showers	$94 \pm 10$
Tirat-Yael	Jan. 18—20, 1959	91	cont. strong showers	$262 \pm 2$ $256 \pm 10$
Rehovoth	Jan. 19—20, 1959	70	cont. strong showers	$163 \pm 3$
Tirat-Yael	Jan. 31—Feb. 2, 1959	75	rain and hail	350*
Rehovoth	Feb. 1, 1959	13	medium showers	$165 \pm 1$
Rehovoth	Feb. 17—18, 1959	46	intermittent showers	$143 \pm 1$
Tirat-Yael	Feb. 18, 1959	33.5	cont. showers	$200 \pm 5$
Rehovoth	Feb. 19, 1959	13.5	cont. showers	$368 \pm 10$ $421 \pm 10$
Tirat-Yael	Feb. 23—24, 1959	60	mixed snow and rain	$210 \pm 1$
Rehovoth	Apr. 4, 1959	5	light shower	$619 \pm 20$
Tirat-Yael	May 17—18, 1959	15	light shower	$537 \pm 5$
Tirat-Yael	Sept. 1958—Jan. 30, 1959	410	composite sample	130*
Lod	Oct. 1958—May 1959	419	rainy season's composite sample	$208 \pm 5$
Beer-Sheva	Oct. 1958—May 1959	162	rainy season's composite sample	260*
Tirat-Yael	Feb. 1, 1959—end of season	300	composite sample	$301 \pm 10$
<i>1959/60 Season</i>				
Tirat-Yael	Sept. 11—15, 1959	17	continuous showers	$64 \pm 4$
Tirat-Yael	Sept. 21, 1959	86	thunderstorm	$72 \pm 4$
Tirat-Yael	Nov. 5—6, 1959	27	shower	$63 \pm 1$
Tirat-Yael	Nov. 15, 1959	19	thunderstorm	$60 \pm 3$
Tirat-Yael	Nov. 28—29, 1959	21	snow and hail	$61 \pm 1$
Prodhromos	Dec. 30—31, 1959	43	showers	$48 \pm 2$
Rehovoth	Jan. 1—3, 1960	40	strong showers	$25 \pm 3$
Prodhromos	Jan. 4—6, 1960	54	cont. strong showers	$31 \pm 0.5$
Rehovoth	Jan. 6—10, 1960	34	cont. showers	$20 \pm 5$
Rehovoth	Jan. 21—24, 1960	65	cont. showers	$27 \pm 2$
Tirat-Yael	Sept. 1959—Feb. 13, 1960	628	season's composite sample	$37 \pm 0.5$
Tirat-Yael	Jan. 23—March 15, 1960	—	composite sample	$46 \pm 3$
Prodhromos	Mar. 7, 1960	21	shower	$42 \pm 0.3$
Tirat-Yael	Mar. 10—11, 1960	255	intermittent showers	$66 \pm 0.2$
Prodhromos	Mar. 21—23, 1960	55	intermittent showers	$68 \pm 0.6$
Tirat-Yael	Mar. 21—23, 1960	130	strong showers	$46 \pm 0.3$
Rehovoth	Sept. 1959—Apr. 1960	250	season's composite sample	$33 \pm 0.6$ $30 \pm 1$
Rehovoth	Jan. 10—Mar. 13, 1960	81	season's composite sample	$44 \pm 0.5$
Prodhromos	Oct. 1, 1959—Jun. 14, 1960	681	season's composite sample	$45 \pm 1$
Nicosia	Sept. 19, 1959—May 1960	284	season's composite sample	$64 \pm 1$

\* Samples with experimental errors in excess of 20%.

TABLE II  
B. RAINWATER COLLECTION (cont.)

Sampling Site	Collection Period	Rainfall Amount (mm)	Sample Description	T. U.
<i>1959/60 Season</i>				
Rhodos	Feb. 6—Apr. 4, 1960	284	season's composite sample	$55 \pm 2$
Yraklion	Feb. 4—May 31, 1960	174	season's composite sample	$95 \pm 1$
Methoni	Feb. 7—May 31, 1960	170	season's composite sample	$64 \pm 1$
Athens	Feb. 1—Jul. 30, 1960	149	season's composite sample	$122 \pm 1$
Adana	Mar. 16—July 31, 1959	161	season's composite sample	$50 \pm 1.5$
Antalya	Mar. 20—July 7, 1959	130	season's composite sample	$107 \pm 2$
<i>1960/61 Season</i>				
Rehovoth	Nov. 1—3, 1960	38	showers	$25 \pm 3$
Tirat-Yael	Nov. 1—6, 1960		showers	$29 \pm 0.5$
Rehovoth	Nov. 27—28, 1960		showers	$31 \pm 1$
Lod	Nov. 1960		monthly composite sample	$24 \pm 1$
Rehovoth	Nov. 1960	75	monthly composite sample	$19 \pm 0.5$
Rehovoth	Jan. 9—11, 1961		continuous showers	$27 \pm 0.4$
Lod	Jan. 1961		monthly composite sample	$24 \pm 2$

TABLE II  
C. SURFACE MEDITERRANEAN SEA WATER

Sampling Site	Collection Period	Rainfall Amount (mm)	Sample Description	T. U.
Near Cyprus	Aug. 31, 1958			$6.9 \pm 0.5$
Off Haifa	Summer 1959			$11.4 \pm 1$
Near Turkish coast	Sept. 1, 1958			$10.3 \pm 1$

in the electrolytic enrichment step was generally better than 5%. A constant ratio of tritium to deuterium enrichment factors was assumed.

The system has not been intercompared with other laboratories; however, standards were obtained by dilution of tritiated water whose specific activity was determined by gas counting in a counter of known efficiency.

## Results

The results of the tritium analysis of rainwater samples are reported in Table II in chronological sequence, together with pertinent meteorological information. For comparison, results of some seawater analyses are also given. The numbers quoted refer to the specific activity at the middle of the collection period. The error quoted in the list, unless otherwise stated, is the statistical counting error. This generally is less than the overall error of about 10%, which takes into account, as well, possible contamination during processing, reproducibility of the enrichment factors during electrolysis and other experimental errors. The results are also graphically presented in Fig. 1.

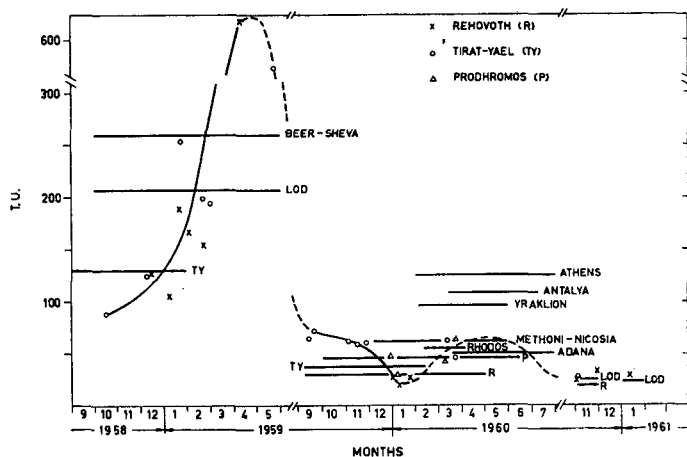


Fig. 1

Tritium analysis of rainwater samples in eastern Mediterranean area. The tritium content of rain showers at Rehovoth, Tirat Yael and Prodhromos and of composite samples of rainwater from other collection stations during 1958–1961. Solid horizontal lines represent results of composite samples at the specified stations. The duration of the collection period is represented by the length of the line.

The following features were immediately apparent from the results:

(a) EFFECT OF RAINFALL AMOUNTS

No statistically valid correlation existed between the measured tritium content of the showers and the rain intensity at Rehovoth or Tirat-Yael stations. However, since all sampled showers were of more than 10 mm/day this conclusion may not apply to smaller rainfall amounts. Three samples of hail and snow at Tirat-Yael also did not give any discordant values. It appeared, however, as if showers from stations with small mean annual rainfall amounts such as Beer-Sheva, Nicosia and Athens showed on the average a higher tritium content than neighbouring stations. This effect will be discussed later.

(b) SEASONAL CHANGES

The highest average tritium concentration during the past five years was encountered during the 1958/59 rainy season. Although individual results scattered, a rise from less than 100 T.U. at the beginning of the season to peak values during April and May of 1959 can be observed.

The tritium values of rain from the 1959/60 season were much lower. The measured values showed a minimum during January 1960 and they rose again in the spring. The few samples from the 1960/61 season which have so far been analyzed showed still lower tritium concentrations, although results were still much higher than the natural cosmic ray levels. It is interesting to note that during the winter of 1960 no change in the tritium levels was observed analogous to the one observed between November 1959 and January 1960.

(c) INTER-STATION DIFFERENCES

The measured tritium content of composite samples from different stations scattered widely. The following procedure was used in order to assess whether these

differences were really due to (average) different activity levels of the rain at the various collecting stations or whether they were merely the manifestation of the different sampling periods and rain distribution. An average tritium activity level  $A_i$  was determined for each month from the experimental curve of the tritium content of single showers for Rehovoth and Tirat-Yael (Fig. 1). The expected average activity level  $\bar{A}$  was then calculated for each composite sample from the known monthly rainfall amounts  $R_i$  at the site during the sampling period according to equation (1).

$$\bar{A}_{\text{calc}} = \frac{\sum A_i R_i}{\sum R_i} \quad (1)$$

These calculated average values, which were based on the assumption that the mean tritium activity levels were the same at Rehovoth and at the other collecting stations, were then compared to the measured ones. The comparison can then be taken as a test for the validity of this assumption.

TABLE III  
MEASUREMENT OF TRITIUM SAMPLES AT DIFFERENT STATIONS

Station	Period	Calculated weighted average T. U.	Measured tritium content T. U.
<i>1958/59 Season</i>			
Lod	Oct. 1958—May 1959	219	208
Tirat-Yael	Sept. 1958—Jan. 1959	128	130
Tirat-Yael	Feb. 1959 to end of season	285	300
Beer-Sheva	Oct. 1958—May 1959	236	260
<i>1959/60 Season</i>			
Rehovoth	Sept. 1959—Apr. 1960	39	31
Tirat-Yael	Sept. 1959—Feb. 13, 1960	34	37
Prodhromos	Oct. 1959—June 1960	48	46
Nicosia	Sept. 1959—May 1960	46	64
Methoni	Feb.—May 1960	52	64
Yraklion	Feb.—May 1960	58	95
Athens	Feb.—July 1960	57	122

The close agreement between calculated and measured values during the 1958/59 season at the Israeli stations is remarkable. Possibly the rain at Beer-Sheva had, on the average, a slightly higher tritium content than the rain from the northern part of the country. The results from the season of 1959/60 showed larger variations; evidently the assumed average values were not as good a measure of the average rainfall. However, the higher average tritium content of the rain from Greece, especially of the Athens rain, was noticeable. The large discrepancy between the two Cyprus stations was also noteworthy; the rain at Nicosia had a definitely higher average tritium content than the rain in North Israel. At first sight it appeared as though the tritium levels at the Cyprus mountain station of Prodhromos conformed to those measured in Israel. However, in all cases where single showers were measured simultaneously both at Prodhromos and Israel the tritium content of the Cyprus rains were higher by 30%—100%.

## Discussion

### SOURCE OF THE DEPOSITED TRITIUM

Any attempt to explain the tritium levels in rainfall at various times and places must take into account the atmospheric residence times and pathways of the tritium injected into the atmosphere.

During the years covered by the present study (1956/61) the following thermonuclear test series were announced:

The United States series "Redwing" and "Hardtack", conducted in the summer of 1956 and 1958 respectively in the Bikini area of the Pacific Ocean. The latter series included two high altitude tests over Johnston Island.

The United Kingdom tests, conducted in May, June and November of 1957 as well as on April 28 and during August and September of 1958 in the Christmas Island area (Pacific Ocean) near the Equator.

The Russian tests, reported to have taken place within the Arctic circle during the autumn of 1957, and again in February-March and October of 1958.

Early results obtained by various authors [2, 6, 7] have indicated an atmospheric residence half-life of a little over one month for most of the tritium injected by thermonuclear explosions into the equatorial atmosphere. This result seems well established. In contrast, the bulk of tritium from polar thermonuclear tests probably remains in the polar stratosphere and will descend into lower air layers of the middle latitudes after a delay of several months [8]. The stratospheric mean life has been postulated by LIBBY [8] to be less than one year. Finally, any tritium which is trapped in the equatorial stratosphere or injected into it by high altitude tests must leak slowly into the troposphere, its stratospheric residence time supposedly being several years. By that time it may be fairly uniformly distributed throughout the lower stratosphere. In fact the higher natural tritium levels which were found in rains following the equatorial tests long after the "decay" of the main pulse were taken as proof of such a leaking stratospheric tritium reservoir [4].

On applying these ideas to the tests conducted during the period under investigation one finds that one cannot expect any direct contribution of tritium from thermonuclear tests conducted during 1956 to the tritium content of rain from the 1956/57 rainy season. The high atmospheric tritium levels from the "Redwing" series were expected in the late summer and since they did not coincide with the local rainy period, they would not primarily influence the results. We may hence take the measured tritium levels of the rainfall of 1956/57 as representing the equilibrium level established here as a result of tritium influx from the stratospheric reservoir into the cloud bearing layers. The experimental value of 50 — 80 T. U. (disregarding the value from the semi-arid station at Tel-Yeruham for reasons to be pointed out later) is about what is found for rain of that period in Chicago [3] and respectively lower and higher than values found in Ottawa [9] and Bern [3].

The measured average tritium values from the 1957/58 season were about the same as during the previous period. Hence, they serve as evidence that no large scale tropospheric transport of tritium into the eastern Mediterranean occurred either from the United Kingdom test of November 1957 or the Russian fall series of the same year. This result, therefore, corroborated Libby's predictions that most of the tritium from the Arctic test sites remained for some time in the stratosphere. The absence of any fallout from the United Kingdom test also seemed reasonable, in view of results of (fission product) fallout measurements in Israel [10, 11] which showed that direct tropospheric transport of air into the Middle East was quite

common from the Russian test sites and also occurred from the Bikini area, but was never found from any of the United Kingdom equatorial tests. Since it so happened that practically no rain fell in Israel after January 1958, nothing was learnt about the tritium values in the spring of 1958 from the year's average.

The detailed results from the 1958/59 season appeared to verify the atmospheric transport models proposed above. The early rain of the season (80 T.U. in October 1958) contained little tritium from either the "Hardtack" test (which had "decayed" by that time), the United Kingdom test of August-September, 1958 or the Russian October series (for reasons previously explained). From February 1959 onwards the tritium level began to rise markedly, in parallel with the increasing amounts of the long-lived components of the fallout in rain at that time. This is shown in Table IV, from which the conclusion may be drawn that the tritium excess in rains during the spring of 1959 resulted mainly from the Russian October series.

TABLE IV  
SPECIFIC ACTIVITY OF FALLOUT COMPONENTS IN RAIN

Date	Long lived fission products ( $\mu\mu\text{c/l}$ at age of 1 yr)*	Sr <sup>90</sup> ** $\mu\mu\text{c/l}$	T. U.
Oct. 15, 1958		3.8	88
Dec. 8, 1958	125	5.0	130
Feb. 1959	260	28.0	225
Apr. 1959	900	—	600
Sept. 1959	195	—	70
Nov. 1959	50	—	60
Mar. 1960	—	4	55

\* These values are from rains of 5-25 mm/d [11] p. 121.

\*\* Determined at the Health Physics Laboratory, Israel Atomic Energy Commission.

It was possible from the synoptic (meteorological) data gathered in the spring of 1959 to make the (tentative) interesting observation that the leakage of stratospheric air took place into middle latitudes and that the high spring tritium levels did not depend on any tropospheric north-south transport. This was shown by the air flow pattern during April and May which was such that rain was brought by westerly air masses, whose north-south component of motion was confined to a rather narrow latitude band. This was in contrast with the flow patterns during February of that year, where much mixing of middle latitude and polar air masses occurred over Europe without, however, causing any "peak" tritium values at that time. The main features of the tritium levels during the 1959/60 season were a decline from values of 65 T.U. in the autumn to around 25 T.U. in midwinter, with a subsequent spring peak. If we assume, for a moment, that the usual fallout pattern due to a stratospheric influx results in a tritium distribution in rain similar to the one observed during the 1960/61 season, i. e. a constant activity level during fall and midwinter and a possible spring rise, we are left with an excess of about 40 T.U. in the fall of 1959. It so happens that if one calculates the residue in fall of 1959 due to the tropospheric "decay" of the 1959 spring peak, assuming a mean half-life of 40 days, one finds exactly 40 T.U. in excellent agreement with the results. A value of 25-30 T.U. was then taken to be the stratospheric component of tritium fallout during the fall of 1959 and the excess of 40 T.U. as being due to the tropospheric "decay" of the spring peak of the year before. As a point of interest, the tritium values reported by LIBBY [12] from Ireland and Bedford (both stations



having maritime properties) did not show higher tritium content of rain in the fall compared to the midwinter of 1959. This discrepancy is what would be expected if BOLIN's interpretation is accepted that the 40 day decay time of a tropospheric tritium pulse is due to re-evaporation of tritium water from land surfaces [4].

The 1959/60 results indicate the presence of a 1960 tritium spring peak. This must be attributed to increased leakage of stratospheric air into the spring troposphere and, unlike the  $\text{Sr}^{90}$  spring peak of that period, cannot be explained by gravitational settling of fallout particles. Results from the spring of 1961 are awaited with great interest in order to see whether this is indeed a recurring seasonal meteorological phenomenon.

The following very approximate values for the average stratospheric contribution to the tritium content of Middle Eastern rain may now be defined, taking into account the fact that the tritium concentration of sea water rose from about 2.5 T. U. in 1956 to somewhat less than 10 T. U. in 1960. A constant "cosmic ray" contribution of 6—8 T. U. was subtracted:

1956/57 season	—	53 T. U.
1957/58 season	—	58 T. U. (almost no spring rains).
1958/59 season	—	200 T. U. (600 T. U. in spring).
1959/60 season	—	18 T. U. (43 T. U. in spring).
1960/61 season	—	13 T. U. (anticipating a small spring peak).

If we take these relative tritium fallout levels as representative of the world-wide levels we can use them to estimate the stratospheric lifetime of tritium. It is immediately evident that this is not constant during the period.

A very short mean stratospheric lifetime of some months was inferred for the tritium from the 1958 October tests, and presumably for all Russian Arctic tests. This conclusion was based on the large difference between the results from spring peaks of 1959 and 1960 and on the large amounts of tritium carried down during 1959.

If we take a tritium level of 58 T. U. as the lower limit of the contribution of equatorially-injected tritium to the stratospheric leakage rate during the 1958/59 season (actually even higher levels were expected due to the intensive testing programme carried out during 1958) one obtains, on comparing the value to the 1959/60 level, an apparent half-life of the order of one year for this material.

The stratospheric mean life, however, apparently increases as the tritium is more evenly distributed throughout the stratosphere, as evidenced by the comparison of the 1959/60 and 1960/61 fallout levels. A mean residence time of three years was obtained for stratospheric tritium during that period. Bomb-produced tritium is expected therefore to come down slowly from the stratosphere for many more years.

These preliminary results indicate that it takes some time until the tritium is equally distributed throughout the stratosphere. Since the descent into the troposphere and stratospheric mixing are competitive processes, one can obtain only lower limits for the stratospheric lifetimes from comparison of the fallout rates at any one place.

#### Meteorological implications of the tritium levels of rain in the eastern Mediterranean Sea area

It is well established that tritium levels increase in an air mass as it moves over land areas, while over the sea dilution occurs by exchange with the sea. As a result,

the tritium levels of rain near the coast are generally low, but they build up as a function of the distance travelled overland.

The tritium levels reported here for rain from the eastern Mediterranean area are characteristic of inland rain levels and are higher than values obtained near the open sea [12]. This may not be so surprising considering the fact that the most common storm track into this area is from the Atlantic Ocean over western Europe into the central Mediterranean, and from there along the sea into the Levant. Thus part of the trajectory of the air which brings rain into this area, lies over continental areas. One could try to explain the lower average tritium content of rain in Israel, compared to the tritium level of rain from Greece, by the exchange process which occurs with sea water as the cloud moves across the eastern Mediterranean Sea. Actually the situation is more complex and the following example illustrates some of the additional factors that come into play.

The synoptic analysis of events preceeding the rain which fell in Israel on December 7—8, 1958 showed that at that time an extensive high pressure belt, which extended across Europe, prevented any air movement from Europe into the Mediterranean. The rain in this case resulted from a depression which had moved slowly along the entire Mediterranean Sea. Here, it seemed, that ideal conditions existed for obtaining rain from a true "maritime" air mass. The high tritium content of this rain (125 T. U.) was, however, at variance with this prediction. Evidently the convergent low pressure system had drawn into its orbit large amounts of air from the continental areas around the sea, which, though containing little water vapour presumably carried a lot of activity with them. One must conclude that the dimensions of the Mediterranean Sea are small compared to the scale of the meteorological processes that determine the tritium content of the air masses moving over it, although the sea modifies these levels to some extent.

Three explanations are possible for the higher tritium content of rain from Cyprus or Greece compared with the levels in Israel.

- (a) The precipitating air mass has different lengths of its trajectory over land and sea surfaces;
- (b) The precipitating air mass is mixed from different proportions of "maritime" and "continental" air;
- (c) Local meteorological factors, such as average cloud height, vapour content of air masses and temperature dependent isotope fractionation effects determine the results.

Meteorological evidence now to be presented, points to (b) as an important factor, although local meteorological peculiarities probably modify the results to some extent.

The typical rain producing pattern of the eastern Mediterranean is schematically described in Fig. 2. One sees an almost stationary convergent system over Greece, southern Turkey or Cyprus (the "Cyprus low") with its associated cold fronts extending into the Mediterranean sea. The rain in the area of convergence, typical for the Cyprus rains, is in contact with larger proportions of continental air masses than the rain which follows in the wake of the cold front (which is typical of the Israeli rain). It is worthwhile emphasizing that a synoptic situation similar to the one described occurred in all cases where rains, simultaneously collected in Cyprus and Israel, gave the higher tritium content for Cyprus rain.

Additional features of the results which one must explain are the relatively low average tritium content of rain at the Cyprus mountain station compared to Nicosia. Quite possibly the rain due to anticyclonic activity, which has been described above

and which has high tritium content, is diluted in the season's composite sample by orographic precipitation which occurs only in the mountains and which may have a lower tritium content.

The somewhat higher tritium content found in rain from the semi-arid regions of southern Israel compared to the one from the northern part of the country may be due to a large proportion of "continental" desert air which is intermixed with the clouds over this site, because of its geographic position.

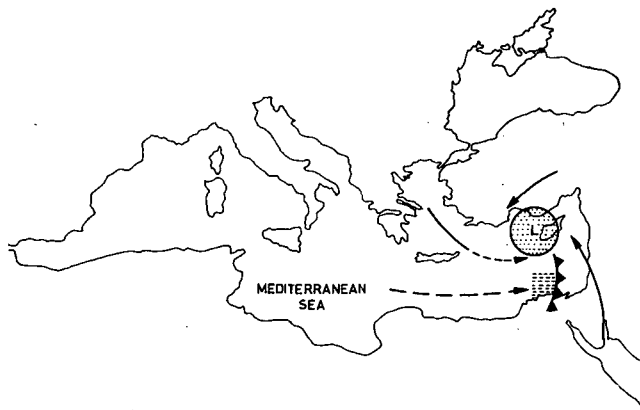


Fig. 2

Typical "rain producing" synoptic situation in the eastern Mediterranean, showing a low pressure region over Cyprus and a cold front extending southwards. Areas of precipitation are indicated by shading. Solid lines represent air flow from continental areas. Broken lines represent air passing over the sea.

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### DISCUSSION III

**F. Begemann** (Federal Republic of Germany): Dr. Gat cited a figure of 10 T.U. for the surface water of the Mediterranean in 1960. Has this value been measured or was it calculated from the average depth of the sea, on the assumption that there is complete mixing?

**J. R. Gat** (Israel): The value is a measured one, based on three water samples from the eastern Mediterranean basin. It is somewhat higher than the figures of 2.5 or 5.5 reported by Prof. Libby in his paper on the central Mediterranean basin. We do not know the reason for the discrepancy between the two results. It may be due to some local circulation pattern. Obviously, many more measurements will have to be taken. However, the absolute values do not greatly affect the picture which we have drawn on the basis of the rain levels, which are much higher anyway.

**W. F. Libby** (United States of America): I am pleased to report that we are remeasuring those surface values for the Mediterranean and that our newer values are higher. Instead of 5 T.U., the new figure is about 7—8, which is much more in line with that reported by Dr. Gat.

**B. Grinberg** (France): Could Mr. Gat give some details on the procedures used for decomposing the tritium and introducing it into the G—M counter?

**J. R. Gat**: The exact procedure was as follows: The zinc powder was introduced into the glass ampoules and properly degassed on a vacuum line. The water was then distilled (by vacuum distillation) into the same ampoules which were then sealed-off and heated in a furnace at over 450 °C for several hours, thereby resulting in the complete decomposition of the sample without any residual water. The ampoules which were provided with break-seals, were then broken on a vacuum line and the hydrogen extracted in the usual way with a Toepler pump and mixed with the counting gas. The method is quite conventional, except that the use of the closed ampoules instead of the open-line zinc furnace minimizes possible cross-contamination of samples.

# THE TRITIUM CONTENT OF ATMOSPHERIC METHANE

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## Abstract — Résumé — Аннотация — Resumen

**The tritium content of atmospheric methane.** The presence of significant amounts of tritium in atmospheric methane is reported. Methane extracted from air samples obtained from various altitudes in the northern and southern hemispheres showed T/H ratios ranging from  $6.3 \times 10^3$  to  $3.4 \times 10^4$  T.U. (1 T.U. equals a T/H ratio of  $10^{-18}$ ) during the period September 1957 to February 1959 and a continuous rise in the southern hemisphere from  $9 \times 10^2$  T.U. in 1953 to  $8 \times 10^3$  T.U. in 1958. Considerable short-term fluctuations were observed at Wembley, England. The tritiated methane distribution in 1958 was consistent with a tropospheric source (or sources) in the northern hemisphere and the Dobson-Brewer model of global stratospheric circulation. The global integral for tritium in the form of atmospheric methane was very roughly  $2.3 \times 10^5$  c in 1958. No satisfactory explanation of the source of the tritiated methane has been found.

**Teneur en tritium du méthane atmosphérique.** Les auteurs signalent la présence de quantités importantes de tritium dans le méthane de l'atmosphère. L'analyse du méthane extrait d'échantillons d'air recueillis à diverses altitudes dans les hémisphères boréal et austral a révélé, pour la période allant de septembre 1957 à février 1959, des taux T/H compris entre  $6,3 \cdot 10^3$  et  $3,4 \cdot 10^4$  U.T. (1 U.T. équivaut à un taux T/H de  $10^{-18}$ ) et, dans l'hémisphère austral, un accroissement continu de  $9 \cdot 10^2$  U.T. en 1953 à  $8 \cdot 10^3$  U.T. en 1958. De fortes variations à court terme ont été observées à Wembley (Royaume-Uni). La répartition du méthane tritié relevée en 1958 était compatible avec l'existence d'une ou de plusieurs sources troposphériques dans l'hémisphère boréal, et avec le modèle de circulation stratosphérique globale de Dobson-Brewer. En 1958, la quantité totale de tritium sous forme de méthane atmosphérique était très proche de  $2,3 \cdot 10^5$  c. Les auteurs n'ont pas pu expliquer de façon satisfaisante la provenance du méthane tritié.

**Содержание трития в атмосферном метане.** Присутствие значительного количества трития в атмосферном метане описано впервые. Метан, извлеченный из образцов воздуха, взятых на различной высоте в северном и южном полушарии, содержал коэффициент T/H, колеблющийся от  $6,3 \times 10^3$  до  $3,4 \times 10^4$  T.U. (1 T.U. равняется T/H помноженному на коэффициент  $10^{-18}$ ), в период от сентября 1957 по февраль 1959 года и продолжающееся увеличение его значения до южного полушария от  $9 \times 10^2$  T.U. в 1953 году до  $8 \times 10^3$  T.U. в 1958 году. Значительные краткосрочные изменения были отмечены в Уэмбли, Англия. Распределение тритированного метана в 1958 году соответствовало тропосферическому источнику (или источникам) в северном полушарии и модели Добсон-Бревера по циркуляции в стратосфере земли. Общее содержание трития в атмосферном метане составляло в 1958 году приблизительно  $2 \times 10^5$  кюри. Не было получено никаких удовлетворительных объяснений появления тритированного метана.

**Contenido de tritio en el metano atmosférico.** Se informa sobre la presencia de cantidades significativas de tritio en el metano atmosférico. El metano extraído de muestras de aire tomadas a diversas alturas en los hemisferios norte y sur presentaba razones T/H que oscilaban entre  $6.3 \cdot 10^3$  y  $3.4 \cdot 10^4$  UT (1 UT equivale a una razón T/H de  $10^{-18}$ ) durante el periodo comprendido entre septiembre de 1957 y febrero de 1959, acusando un aumento continuo en el hemisferio sur, en el que se pasó de  $9 \cdot 10^2$  UT en 1953 a  $8 \cdot 10^3$  UT en 1958. En Wembley (Inglaterra) se observaron

considerables fluctuaciones en plazos breves. La distribución del metano tritiado observada en 1958 es compatible con la existencia de una o varias fuentes troposféricas en el hemisferio norte y con el modelo Dobson-Brewer de circulación estratosférica global. La cantidad total de tritio en el metano atmosférico fue del orden de  $2.3 \cdot 10^5$  c en 1958. El origen del metano tritiado no puede explicarse satisfactoriamente.

## Introduction

Tritium has been shown to exist in the atmosphere in two forms. The presence of natural tritium was first detected in atmospheric hydrogen by FALTINGS and HARTECK [1] and was later shown to be present in rainwater by GROSSE *et al.* [2].

Since the beginning of thermonuclear weapon tests a large quantity of man-made tritium has been injected into the atmosphere. This has caused a rise in the tritium content of rainwater from a level of between 0.5 and 5 T. U. [2, 3] to peak values as high as 500 T. U. [4]. (1 Tritium Unit (T. U.) equals a ratio of 1 tritium atom to  $10^{18}$  atoms of hydrogen). Tritium in water has proved to be a particularly valuable tracer substance in the study of water circulation patterns. Simultaneously with the increase in the tritium content of rainwater there has been an increase in the amount of tritium present in atmospheric hydrogen from a value of  $3.8 \times 10^3$  T. U. in 1948/49 [1] to  $4.9 \times 10^5$  T. U. in 1959 [5] though the source of this tritium is uncertain and it does not appear to be directly related to thermonuclear tests [6].

Air contains approximately 1.2 parts per million of methane [7]. Since tritium had already been detected in atmospheric hydrogen and in rainwater, it appeared of interest to determine whether atmospheric methane also contained a significant quantity of tritium. Furthermore, a proposal had been made to release tritiated methane as a tracer gas for atmospheric circulation studies during the International Geophysical Year. Hence it was clearly of importance to establish the level and distribution of any tritiated methane which might already exist in the atmosphere.

## Experimental

### ORIGIN OF SAMPLES

Atmospheric methane was extracted from the following types of samples:

- (a) Samples of air collected by aircraft flying at various altitudes over the United Kingdom, Singapore, northern and southern Australia. Air was taken from the compressor of the aircraft jet engine;
- (b) Samples of ground level air collected at Singapore, in northern and southern Australia, and in the south Atlantic Ocean;
- (c) Samples of crude atmospheric oxygen extracted several years previously by oxygen plants situated in Kenya and New Zealand;
- (d) Samples of ground level oxygen which had been further enriched in methane by distillation, supplied by British Oxygen Gases Ltd. from their plant at Wembley, Middlesex;
- (e) One sample of methane produced by the anaerobic decomposition of sewage, obtained from the Mogden Purification Works, Isleworth, Middlesex.

### EXTRACTION OF METHANE FROM SAMPLES

#### (a) Air samples

The samples were received in cylinders holding about 500 ft<sup>3</sup> of air. Air contains about 1.2 ppm of methane by volume, hence each cylinder contained about 14 cc

of methane. The methane extracted from a number of cylinders was combined to provide a sample large enough for counting.

After extraction of carbon dioxide and water vapour by passing the air through a cooling coil and filter, both immersed in liquid oxygen, a preliminary concentration of the methane was achieved by passing the air at a flow-rate of about 300 ft<sup>3</sup> through a column of activated charcoal, 1½ in diameter, and approximately 7 ft long, immersed in liquid oxygen. After the air had passed through, the column was allowed to warm up progressively from the inlet in sections and the impure methane, together with other absorbed gases was swept forward by a stream of nitrogen into the final section of the bed. Finally, this section was heated and the methane together with about 6 l of oxygen and nitrogen was driven into a smaller charcoal chromatographic column ¼ in diameter and 3 ft long, also cooled in liquid oxygen. The temperature of this column was allowed to rise by natural convection, and the absorbed gases were eluted from the column with a stream of hydrogen at 500 cc/min. Oxygen and nitrogen were driven off first, followed a short while later by the methane, the emergence of the various gases being indicated by a thermal conductivity detector.

The methane still contained a certain amount of impurity and final purification was achieved by a further gas chromatographic separation using a column of "Linde" Molecular Sieve 5A, ½ in diameter and 6 ft long, immersed in an ice-bath. The emergence of the methane was again indicated by a thermal conductivity detector and the gas was finally trapped in a glass trap cooled in liquid nitrogen. The hydrogen was carefully pumped off the methane and the volume of methane measured. Overall recovery was approximately 85% and the methane contained less than 0.2% impurity by mass-spectrometric analysis.

#### (b) *Oxygen samples*

The crude oxygen samples from plants in Kenya and New Zealand were processed in a similar manner to the air samples, except that in order to prevent condensation of liquid oxygen in the charcoal column, the samples were diluted with four times their own volume of high purity nitrogen.

The oxygen samples received from British Oxygen Gases Ltd., Wembley contained sufficient methane to enable the preliminary enrichment to be dispensed with. The gas was passed into the molecular sieve column immersed in liquid oxygen, after which it was allowed to warm up, and the gases eluted with hydrogen, the methane being collected as before.

#### (c) *Sewage methane*

The main impurities in the sewage methane were carbon dioxide and air. The carbon dioxide was removed by passing the gas through a trap immersed in liquid oxygen, and the air by repeated freezing in liquid nitrogen and pumping.

#### MEASUREMENT OF TRITIUM ACTIVITY

A proportional counter filled with the methane was mounted in a low background counting equipment comprising an 8 in steel shield, an anticoincidence array and inside a further shield of 1 in of redistilled mercury. The background of the 350 cc volume counter used for most of the determinations was  $2.9 \pm 0.2$  cpm. Counting rate for samples varied between 3 cpm and 20 cpm. Corrections for wall loss, end loss and bias loss were made in determining the efficiency of the counter which was about 80%. Energy calibration was by means of a 6 keV manganese X-ray source

covering a 0.02 in thick beryllium window in the counter wall. Observation of the energy spectrum of the atmospheric methane activity showed an end point close to 18 keV, the maximum energy of tritium beta particles. In addition, to confirm that tritium was the main source of the observed activity, and to estimate the contribution due to  $C^{14}$ , a measured sample of atmospheric methane was burned to carbon dioxide which was subsequently counted for  $C^{14}$ . A combined sample of atmospheric methane composed of samples covering a period of several months and which had a specific activity of 0.203 dpm/cc gave an activity when burned to carbon dioxide of 0.0068 dpm/cc. This last figure is equivalent to 12.7 dpm/g of carbon which corresponds to a  $C^{14}$  age of less than 200 years in agreement with a measurement of atmospheric methane by LIBBY, reported by GLUECKAUF [7]. The measured specific activities of all the methane samples were corrected by making allowance for the presence of the  $C^{14}$  activity, and also by allowing for the decay of tritium during the period between sampling and measurement.

#### ERRORS

The errors quoted in the results include estimates of the error due to measurement of gas volume counted, variation of counter background, uncertainty in counter efficiency, and statistical counting errors. In addition, there are possible errors due either to dilution of the methane with extraneous methane of different tritium content, or to isotopic exchange with hydrogen or water of different specific activity.

The  $C^{14}$  activity of the methane collected agreed with that of contemporary carbon within the experimental error. Hence significant contamination of the atmospheric methane by methane derived from sources containing "dead" carbon did not occur. This excludes methane from coal mines, from cracking of hydrocarbon fuels or from cracking of the lubricating oils in the compressors used for collecting the samples. As a further check on this last possibility, measurements were made of the carbon dioxide abundance of the air after compression in cylinders, since any cracking of the lubricating oil would also have been accompanied by oxidation. The abundance of carbon dioxide in the compressed air was the same, within the experimental error (1 ppm) as that of the atmosphere sampled at the time of collection.

Contamination from local biological sources such as the anaerobic decomposition of organic matter cannot be excluded on the basis of the  $C^{14}$  measurement. However the possibility of local biological sources affecting the air samples collected at 20 000 ft and above is obviously remote. Moreover the measured abundance of methane in the air samples, taking into account losses in the apparatus, ranged from 1.0 to 1.2 parts per million by volume, averaging somewhat less than the figure of 1.2 ppm given by GLUECKAUF [7]. Evidently gross contamination of the air samples with biological methane did not occur.

The agreement between the tritium abundance in air samples collected at 25 000 ft over the United Kingdom and the ground level oxygen samples collected at Wembley during the same period (Fig. 2) shows that significant contamination of these oxygen samples by biological methane also did not occur.

The possibility of extraneous methane arising from either the nitrogen or the hydrogen used in the preparation of samples or from reaction between hydrogen and the charcoal column was ruled out by blank experiments carried out with pure nitrogen and hydrogen only. The possibility of isotopic exchange during the processing was investigated by passing methane samples of zero and of known tritium abundance through the processing equipment from time to time. In no case was any change of the tritium abundance detected.



## Results and Discussion

The measurements of tritium abundance in atmospheric methane are presented in Table I, except for the oxygen samples collected at Wembley, the results of which are shown in Fig. 1.

TABLE I  
ABUNDANCE OF TRITIUM IN ATMOSPHERIC METHANE

Sample Location	Altitude (ft)	Sampling Period	Mean Sampling Date	Tritium Abundance (T. U. $\times$ 1000)
South Atlantic Ocean	0	20/2/57–22/3/57	7/3/57	$4.0 \pm 0.6$
South Atlantic Ocean	0	17/11/57–22/4/58	9/3/58	$6.3 \pm 1.0$
New Zealand	0	29/7/53	29/7/53	$0.87 \pm 0.15^*$
Southern Australia	0	16/9/57–11/7/58	6/2/58	$7.7 \pm 1.0$
Southern Australia	0	14/9/58–17/10/58	1/10/58	$8.7 \pm 1.0$
Southern Australia	20 000	15/9/57–2/7/58	6/2/58	$6.5 \pm 1.0$
Southern Australia	20 000	15/9/58–14/10/58	30/9/58	$9.6 \pm 1.0$
Southern Australia	40 000	16/9/57–10/7/58	6/2/58	$6.3 \pm 1.0$
Southern Australia	40 000	14/9/58–15/10/58	30/9/58	$8.5 \pm 1.0$
Northern Australia	40 000	16/9/57–15/3/58	1/1/58	$7.9 \pm 1.0$
Kenya	0	4/7/55–15/7/55	10/7/55	$2.6 \pm 0.4^*$
Singapore	0	25/6/58–10/7/58	3/7/58	$13.6 \pm 2.0$
Singapore	20 000	30/6/58–10/7/58	5/7/58	$12.9 \pm 2.0$
Singapore	40 000	1/7/58–9/7/58	5/7/58	$11.4 \pm 2.0$
United Kingdom	25 000	10/9/57–26/9/58	18/3/58	$23.0 \pm 2.0$
United Kingdom	25 000	30/12/57–3/4/58	16/2/58	$19.5 \pm 2.0$
United Kingdom	25 000	11/11/58–1/12/58	21/11/58	$23.0 \pm 2.0$
United Kingdom	47 000	9/9/57–26/9/58	18/3/58	$7.6 \pm 1.0$
United Kingdom	47 000	24/3/58–25/3/58	25/3/58	$8.7 \pm 1.0$
United Kingdom	47 000	3/11/58–5/12/58	19/11/58	$8.8 \pm 1.0$

\* Oxygen Samples.

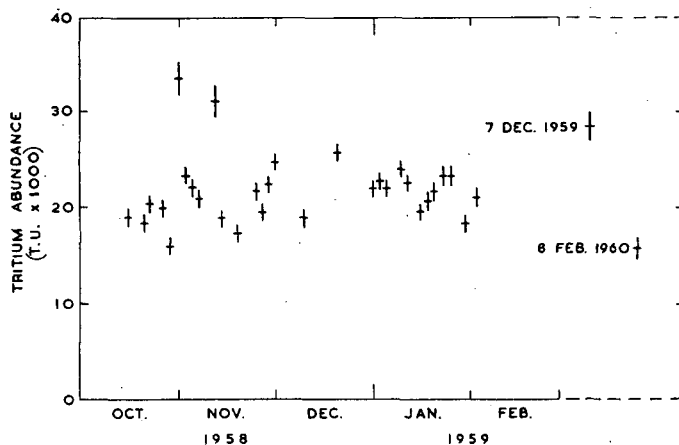


Fig. 1

Abundance of tritium in atmospheric methane sampled at Wembley, Middlesex.

Since the atmosphere is well mixed in the east-west direction due to the prevailing circulation the concentrations throughout the globe may be shown on an altitude-

latitude diagram as in Fig. 2, where the average values for the period September 1957 to February 1959 are plotted.

The abundance in the stratosphere in the middle northern latitudes was less than 40% of that in the troposphere at the same latitude and was closer to the value found near the equator at about the same height. The distribution of tritium activity

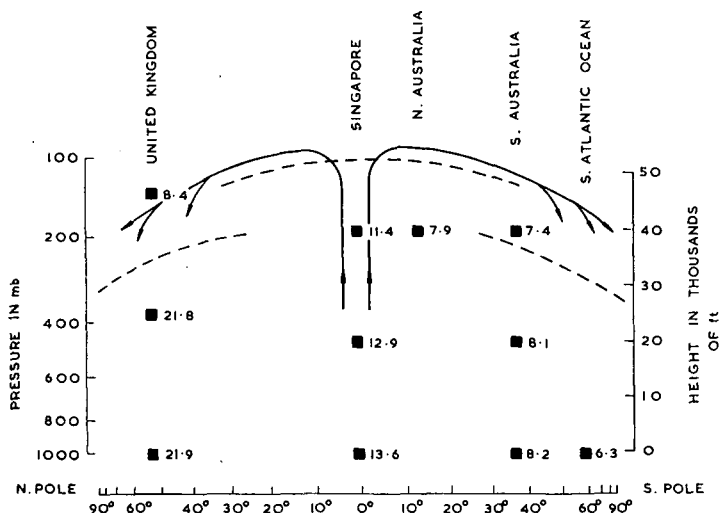


Fig. 2

Average abundance of tritium (T. U.  $\times 1000$ ) in atmospheric methane during the period Sept. 1957 to Feb. 1959. The dotted lines represent the tropopause and arrows show direction of atmospheric circulation after DOBSON and BREWER [9, 10].

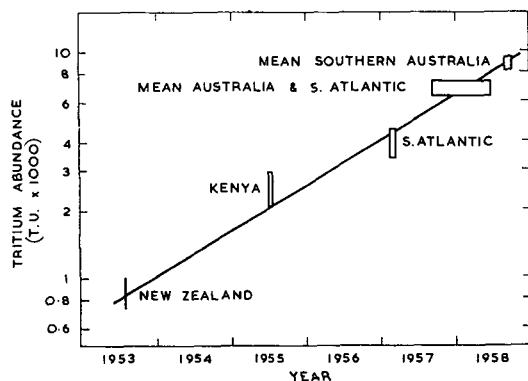


Fig. 3

Growth of tritium abundance in atmospheric methane in the southern hemisphere.

in 1958 was consistent with a source of tritiated methane in the northern hemisphere troposphere and also with the DOBSON-BREWER [9, 10] model of global stratospheric circulation, the main features of which are shown in Fig. 2. On this model upward diffusion from the troposphere at temperate latitudes is prevented by the slow sinking of air in the lower stratosphere. This air has risen through the tropopause

near the equator and spread out northwards. Thus the tritium activity in the stratosphere at a latitude of  $50^{\circ}\text{N}$  is expected to be similar to that at the equator.

In the southern hemisphere the tritiated methane present in equatorial air is fed into both the troposphere and the stratosphere so that we should expect the abundance to be approximately the same in each.

In Fig. 3 is plotted the abundance of tritium in atmospheric methane for the years 1953/58 for various places in the southern hemisphere. Since Fig. 2 shows that the tritiated methane is fairly uniformly distributed in the southern hemisphere, we are justified in regarding the measurements at different places in the southern hemisphere as representative of the whole hemisphere at the time of sampling. The results from Kenya have been included, even though Kenya lies to the north of the equator, since at the time of sampling the station was in the southern meteorological hemisphere. It may be seen that the tritium abundance in atmospheric methane has risen from 900 T. U. in 1953 to 8000 T. U. in 1958 and that over this period the growth may be approximately represented as being exponential, the line drawn on the figure having a doubling time of eighteen months.

MACHTA [12] has examined theoretically the global dispersion of fission products released at an exponentially increasing rate from a number of sources situated in the temperate latitudes of the northern hemisphere. He shows that for the case where no deposition occurs, as applies to tritium in atmospheric methane, the concentration at any latitude of the globe also rises exponentially with the same doubling time once the initial transient period equivalent to one or two doubling periods has elapsed. We assume therefore that the tritium activity in methane has been rising throughout the globe with an approximate doubling time of eighteen months in the period 1953 to 1958.

BURTON and STEWART [11] have shown from radon decay product measurements that the time taken for stratospheric air to travel from the equator to a latitude of  $50^{\circ}\text{N}$  is about six months. The tritiated methane abundance of the lower stratospheric air over the United Kingdom should therefore correspond with that in equatorial air some six months previously. From Fig. 2, taking a value of  $1.14 \times 10^4$  T. U. for the abundance in equatorial air, and a doubling time of 18 months we should expect the abundance six months previously to have been  $9.0 \times 10^3$  T. U. which is in reasonable agreement with the value of  $8.4 \times 10^3$  T. U. found for United Kingdom stratospheric air, bearing in mind the averaging of samples over the period.

The results for Wembley, presented in Fig. 1, show considerable short term variations in the tritium abundance, and this too is consistent with a tropospheric source in the northern hemisphere. Back-tracking of the movement of surface air reaching Wembley on the date of the two highest abundances (31 October 1958 and 10 November 1958) suggested a source or reservoir in a general north-westerly direction, though such methods do not yield very precise information. Since only two measurements were made at Wembley near the beginning of 1960 and owing to the short term fluctuations, it is not possible to say whether the growth exhibited in the southern hemisphere between 1953 and 1958 continued in the northern hemisphere between 1958 and 1960.

A very approximate estimate of the total tritium present in methane throughout the whole atmosphere has been made by assuming that the mean northern hemisphere tropospheric abundance is equal to the average of the United Kingdom and Singapore values and that the abundance is uniform throughout both the northern hemisphere stratosphere and the whole of the southern hemisphere. The tritium

TABLE II

ABUNDANCE OF TRITIUM IN THE NORTHERN HEMISPHERE TROPOSPHERE  
AND ESTIMATED ATMOSPHERIC WORLD INTEGRAL OF TRITIUM IN VARIOUS  
FORMS IN 1958

Form	Abundance (T. U.)	Atmospheric Integral (c)
Atmospheric Hydrogen [5]	$2.5 \times 10^6$	$2 \times 10^6$
Atmospheric Methane	$2.2 \times 10^4$	$2 \times 10^6$
Rainwater [4]	60 with peaks to 500	$2 \times 10^8$

inventory thus calculated for 1958 was about  $2.3 \times 10^6$  c. In Table II, the abundance of tritium in atmospheric methane is compared with that in atmospheric hydrogen, and in rainwater, for 1958. Also shown are estimates of the world integral of tritium in each of these three forms present in the atmosphere. It is evident that while the bulk of tritium is present in rainwater, the specific activities of both methane and hydrogen are several powers of 10 higher.

#### Source of tritiated methane

We are unable to suggest any satisfactory explanation for the source of this tritiated methane. We can obviously rule out natural sources for the tritium in atmospheric methane both on account of the non-uniform distribution throughout the globe and the continuous growth which has occurred in the past several years.

It also seems unlikely that any tritiated methane would be produced in a thermonuclear weapon test, due to the high temperatures and oxidizing conditions prevailing. Furthermore we should expect the concentration in the stratosphere to be higher than that in the troposphere, the converse of that actually found. The possibility of exchange of weapon-produced tritium found in rainwater with atmospheric methane to produce tritiated methane is unlikely on account of the much lower specific activity of the tritium in rainwater as shown in Table II.

Biological processes will convert some of the tritium found in rainwater into tritiated methane. However, the sample of sewage methane measured by us had a tritium abundance of less than 100 T. U. (the limit of detection) so that concentration of the tritium sufficient to give the values of 1000 T. U. and above observed in atmospheric methane evidently does not occur by this mechanism.

Isotopic exchange between atmospheric hydrogen and methane is a mechanism which could lead to methane of sufficiently high tritium abundance. However, it has been shown [8] that deuterium (and hence presumably tritium also) exchanges with methane at a measurable rate only above  $450^\circ\text{C}$ .

It appears that the tritiated hydrogen also present in the atmosphere may be derived from the same source, as BISHOP and TAYLOR [5] have shown that in the northern hemisphere, this too has been rising exponentially during the past decade with a doubling time of eighteen months, the same as that of methane.

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#### DISCUSSION IV

H. E. Suess (United States of America): I should like to present some data on atmospheric methane which will supplement the paper of Dr. Eggleton. About two years ago, Prof. Libby and I considered whether it would be worth including the measurement of tritium in atmospheric carbon-14 in our programmes. We did not know of the extensive work that was going on in the United Kingdom — otherwise we would probably not have planned to do anything ourselves. So far we have investigated only one sample, a very large one, which we obtained from the Linde plant at Gary Indiana. We expected that methane samples obtained from this highly-industrialized area would contain an appreciable fraction derived from city gas, automobile exhausts and other artificial sources. Measurement of all the isotopes of the methane might make it possible to correct for industrial methane, but this is not yet feasible on the basis of the results obtained from the one sample. We have measured the carbon-14 rather accurately at La Jolla and found it to be about 74.6% of our standard wood sample (a 19th century wood corrected for decay). Dr. Craig at La Jolla measured the carbon-13, which was 39.6 per mill relative to the Chicago PDB standard. This means it was somewhat lighter, or in the range of the lightest woods that occur in nature. The deuterium was measured by Irving Friedman at the United States Geological Survey and was found to be 4% below that of Lake Michigan standard water. The tritium was measured just recently by Mr. Bainbridge at La Jolla and independently by Dr. Begemann at Mainz. The results of both laboratories were identical, i. e. 19 600 T. U. The tritium result is in excellent agreement with the average obtained by the British laboratories. The carbon-14, however, is considerably below that of present-day carbon dioxide in the atmosphere, which is not quite what one would expect if the British samples had a carbon-14 content equal to that of present-day carbon-dioxide. We would therefore have to conclude that our sample was diluted with "dead" carbon containing methane, as we might have expected, considering that the source came from an industrial area. In that event, our very close agreement in the tritium value would be rather difficult to understand. Seeking an explanation, we thought that we could learn something about the origin of the tritium in the atmospheric hydrogen by looking at the methane. We still think that this might be possible eventually. We had suspected that the tritium might get into the stratospheric methane through photochemical processes, but this explanation presents several difficulties, especially since the methane was found to contain less tritium higher up than at sea level. There is certainly no question of the methane representing a steady equilibrium at a high atmospheric level, because in that case the carbon-14 content would have to be at least twice as high as that actually found (the carbon-14 content of the stratosphere being about twice as high as in

surface carbon dioxide). I agree that at present we cannot point conclusively to a source for the tritium in the methane, but if we had a few more samples measured for carbon-13 and deuterium as well, we could then probably distinguish between several sources of methane that are possibly mixed together in the way we expected. I very much hope that the work will be continued in Britain. We ourselves are now planning to do a few more samples, although we have to depend on the supply of tritium from liquid air plants and have not tried Dr. Eggleton's technique. In that connection, I would like to ask him how he separated the tritium or rather, the methane, from the atmospheric krypton, which has a fairly high radioactivity. We found it necessary to burn the methane to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and then resynthesize the counting gas from it.

**A. E. J. Eggleton** (United Kingdom): As regards the accuracy of our carbon-14 measurement, I should emphasize that we used a large sample ( $\text{CO}_2$  volume 740 cc) obtained from a combination of a number of methane samples used in the tritium measurement. I should also point out that we are not a carbon-14 dating laboratory, so that we do not have any standards or other measurement safeguards. We estimate the error to be less than 10%. Our measurement is in agreement with an earlier one of Prof. Libby on a sample of atmospheric methane obtained from the United Kingdom and — I believe — from the same source of the samples referred to in our paper. He is quoted by GLUECKAUF [7] as saying that the carbon-14 age of this methane was something less than 200 years, a finding which is more in line with our measurement than that cited by Prof. Suess. It may be that the sample collected by Prof. Suess was somewhat contaminated by local sources of "dead" methane. The date of his sample is December 1959. If his figure of 19 600 T. U. in atmospheric methane is adjusted for such contamination, the revised figure of 26 100 T. U. falls close to the value of 28 500 T. U. which we measured at Wembley at about the same time. Unfortunately we did not make it clear in our paper that the  $\text{C}^{14}$  measurement was done on samples of methane extracted from the gas supplied by British Oxygen Gases Ltd. at Wembley, Middlesex. We were not able to collect enough methane to enable us to make a  $\text{C}^{14}$  measurement on stratosphere methane so that we have no evidence on the question of whether stratospheric methane is in steady-state equilibrium with the carbon dioxide, as was implied by Prof. Suess in his remarks.

As to the second question, concerning the separation of atmospheric krypton from the methane, it was done on the Molecular Sieve 5 A column. We knew from some French measurements that there was a certain amount of activity in the krypton, so we were careful to avoid any contamination from this source. Actually, the krypton peak was well separated from that of the methane and therefore the degree of contamination was negligible, as shown by the mass spectrographic analyses of the methane.

**D. Lal** (India): Has Dr. Eggleton considered the possibility of getting tritiated methane in the atmosphere from reactors — presumably by biological processes (i.e. by biological conversion of the tritiated water to methane)?

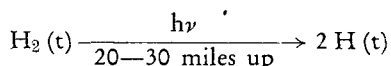
**A. E. J. Eggleton:** We did consider this as a possible source, but it is extremely difficult to make any reliable calculation because the relevant data for all the world's reactors are simply not available. We took a measurement on the BEPO reactor at Harwell and found virtually no tritiated methane in the effluent from it, but of course BEPO is not a particularly representative reactor so that one should not place too much reliance on this measurement. To calculate the amount

of tritiated methane from this source, we would need adequate information about other types of reactors. You have suggested a biological process. Of course, this is a possibility but rather high tritiated water levels would be required to give the specific activities we have observed, and we know from other measurements that the tritium in water is dispersed quite rapidly.

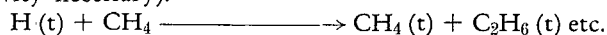
**D. Lal:** I should like to ask Prof. Suess whether it would be possible at present to get pre-1950 atmospheric methane samples.

**H. E. Suess:** Unfortunately, I have no other sources available. I do not think it would be possible to obtain any measuring samples other than those we have had all along.

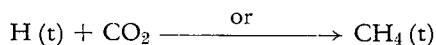
**J. G. Burr** (United States of America): I would like to comment on the origin of the labelling in the methane. In view of the known fact that atoms are formed in the upper atmosphere, hydrogen atoms so formed can exchange with methane quite rapidly and they can also reduce carbon-dioxide to methane. From the relative activities, it is apparent that the labelling in the methane comes from the hydrogen, or vice versa, and not from the water. We also know that hydrogen atoms formed in the dissociation of hydrogen gas cannot react easily with water molecules. That reaction is very difficult. This would account for the fact that the water is not labelled as highly. It is suggested that the mechanisms involved are as follows:



(the reaction  $\text{H}_2\text{O} \xrightarrow{h\nu} \text{H} + \text{OH}$  does not provide H atoms with the high specific activity necessary).

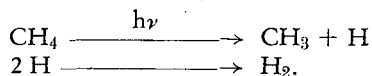


This reaction proceeds readily [STEACIE, "Atom and Free Radical Reactions", etc.].



This reaction proceeds readily in the presence of an electric discharge or alpha particle radiation [LIND, "Effect of alpha, beta and gamma particles on gases" (ACS monograph)].

Conversely, the methane may be the origin of the labelling in the hydrogen:



The reaction



is known to be very endothermic and thus very slow. This accounts in part for the lack of high specific activity in water vapour from the hydrogen atom processes.

Much of the work on the action of tritium recoil atoms (Rowland — Wolfgang) is pertinent.

**A. E. J. Eggleton:** There is certainly a possibility that tritiation occurs from the hydrogen. One point that I did not bring out in my presentation was the fact that the level of tritium in atmospheric hydrogen has been rising with about the same doubling time as methane and this certainly suggests that they are related in some way. However, it seems to me that the mechanism suggested by Mr. Burr suffers from the difficulty mentioned by Prof. Suess, namely, that the concentrations are the wrong way round: we get too little in the stratosphere and I would

not think that such a mechanism had any chance of operating in the troposphere, although I may be wrong.

**J. G. Burr:** If this labelling takes place, it does so at altitudes of perhaps 20—30 miles, whereas your measurements were, I believe, made at much lower altitudes. Thus, the methane is formed very high up while your concentrations are from very low down. The two need not necessarily be related.

**J. Varshavsky** (Union of Soviet Socialist Republics): Would Dr. Eggleton agree with the suggestion that the presence of the tritium in the methane is due to an isotopic exchange between the gaseous hydrogen of the atmosphere and the methane, caused by the action of cosmic rays or simply of hard radiation in the upper layers of the atmosphere? In such a case the exchange would not necessarily have to be able to attain equilibrium, owing to which fact the ratio of the tritium content in the hydrogen and in the methane does not have to be strictly constant. The essential consideration here is that as the hydrogen and methane, moving downward from the upper layers, enter the atmosphere, the exchange slows down radically or comes to a complete halt, owing to the decrease in the intensity of radiation. This type of isotopic exchange of hydrogen between gaseous deuterium and saturated hydrocarbons in the presence of radiation (in particular gamma radiation) actually does occur, as we have seen in one of the papers on the exchange of deuterium. This suggestion may enable you to explain the presence of tritium in methane which you observed.

**A. E. J. Eggleton:** I think there is the same objection as there is to the suggestions made by other speakers concerning a possible transfer of tritium from atmospheric hydrogen and water to methane by mechanisms which can only operate in the stratosphere (photo-dissociation of hydrogen, cosmic ray processes, etc.). should point out that our measurements for the United Kingdom stratosphere upon which we base our postulation of a tropospheric rather than a stratospheric source for tritiated methane consist of three independent determinations (Table I of our paper, United Kingdom, 47 000 ft), each of which was made on a combined sample collected over a period. From measurements of the height of the tropopause, we are satisfied that on each occasion the samples were actually collected in the stratosphere. We consider therefore that we have established with reasonable certainty that the source of the tritiated methane is in the troposphere (northern hemisphere) and that we can rule out any stratospheric mechanism, at least as a major contributor. In other words, any mechanism which is at work mainly in the stratosphere apparently does not fit the facts of the experiment.

**E. Roth** (France): If it were possible to measure the isotopic composition of the methane and hydrogen and to determine their deuterium content, there would be a basis for confirming or disproving Dr. Varshavsky's hypothesis that the tritium in the methane is due to an exchange in the stratosphere. According to the figures given by Dr. Eggleton the tritium activity of the methane could be satisfactorily explained if the isotopic exchange between hydrogen and methane was within a few per cent of the value at equilibrium, because if the figures are correct the atmosphere and the stratosphere should contain approximately the same number of atoms in the form of hydrogen and of methane. The equilibrium constant would be 2—4 (closer to 2 for deuterium, closer to 4 for tritium). Therefore the amount of tritium found in the methane represents only a few per cent of the total equilibrium value. But these few per cent would be the same for deuterium and could probably be measured. Isotopic analysis for deuterium is sufficiently accurate



to make it possible to detect a few per cent of exchange in a reaction in which a factor of 2—3 may be expected at equilibrium.

**A. E. J. Eggleton:** I am sorry to say that we did not make any measurements of the deuterium concentration of our methane, so we are unable to give that information. Unfortunately, we no longer have any of the methane samples, as the programme is not continuing. The only measurement of this is the one made by Prof. Suess.

**H. E. Suess:** The figure for the deuterium we have is only slightly lower than that for standard water and is comparable to that of water vapour or snow. It is far from any exchange equilibrium. However, the same is true of the hydrogen in the atmosphere where the deuterium is completely out of equilibrium and the concentration is close to that of the water vapour.



# TRITIUM IN METEORITES AND IN RECOVERED SATELLITE MATERIAL

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Abstract — Résumé — Аннотация — Resumen

**Tritium in meteorites and in recovered satellite material.** Tritium was measured in separated phases and in whole rock samples of the Bruderheim chondritic meteorite and in samples of lead and iron material of recovered satellites. Radioactive isotopes of argon were also measured. The tritium and argon radioactivity in the Bruderheim meteorite can be reasonably well explained by the interaction of cosmic ray particles of some thousand million volts energy with the meteoritic material. The tritium content of the recovered satellite material was more than a factor of a hundred too large to be explained by the interactions of cosmic rays or by the interactions of solar flare particles with the satellite. The high tritium content of the satellite material must result from a flux of incident tritium particles that stop in the satellite.

**Tritium dans les météorites et dans les matières provenant d'un satellite récupéré.** On a mesuré la teneur en tritium d'échantillons de diverses parties et de l'ensemble de la roche formant la chondrite de Bruderheim, ainsi que celle d'échantillons de plomb et de fer prélevés sur des satellites récupérés. On a également mesuré la teneur en radioargon dans la météorite de Bruderheim. La présence de tritium et de radioargon peut fort bien s'expliquer par l'interaction d'éléments de la météorite et de rayons cosmiques corpusculaires ayant une énergie de l'ordre du milliard de volts. La teneur en tritium des satellites récupérés était plus de cent fois trop élevée pour pouvoir être expliquée par une interaction entre les rayons cosmiques ou les particules provenant d'éruptions solaires et le satellite étudié. La forte teneur en tritium des matières provenant des satellites est certainement due à un flux incident de particules de tritium qui sont retenues dans le satellite.

**Тритий в метеоритах и в возвращенном спутнике.** Содержание трития было измерено в отдельных частях и целых образцах камня гранулированного метеорита Брудерхейма, а также в образцах свинца и железа, взятых с возвращенных спутников. Были также измерены радиоактивные изотопы аргона. Тритиевая и аргонная радиоактивность в метеорите Брудерхейма может быть вполне определенно объяснена взаимодействием с метеоритным веществом частиц космических лучей с энергией в несколько тысяч миллионов вольт. Содержание трития в материале возвращенного спутника было более на коэффициент 100, что является слишком большой величиной, чтобы объяснить это взаимодействием космических лучей или взаимодействием испускаемых солнцем раскаленных частиц со спутником. Высокое содержание трития в материале спутника является непосредственным результатом бомбардировки потоком случайных тритиевых частиц, которые оседают в материале спутника.

**Tritio en meteoritos y en el material de un satélite recuperado.** Se midieron las concentraciones de tritio en fases separadas y en muestras enteras de roca del meteorito condritico de Bruderheim, y en muestras de plomo y de hierro de satélites recuperados. También se determinaron las concentraciones de los isótopos radiactivos del argón. La radiactividad correspondiente al tritio y al argón en el meteorito de Bruderheim se explica satisfactoriamente por la interacción de partículas de rayos cósmicos de varios miles de millones de electrón-voltios de energía con el material meteorítico. El contenido de tritio del material de los satélites recuperados era más de cien veces superior al que se puede explicar por la interacción con el

satélite de rayos cósmicos o de partículas procedentes de erupciones solares. La elevada concentración de tritio hallada en el material del satélite tiene que ser resultado de un flujo de partículas incidentes de tritio que quedan detenidas en el satélite.

### Tritium production by energetic protons

When protons with sufficient energy strike a material (usually called a target), tritium and other isotopes are produced. A particular isotope is produced when the combined mass of a target atom and a proton is heavier than the mass of the isotope. The production rate or cross-section depends on the type of target material and the energy of the incident proton. The cross-section [1] for the production of tritium in iron is 7.2 mb for 160 MeV protons, 60 mb for 1000 MeV protons, 90 mb for 3000 MeV protons, and 110 mb for 6200 MeV protons. The cross-section for the production of argon-37 in iron is 0.19 mb for 160 MeV protons, 4.7 mb for 1000 MeV protons and 6.7 mb for 6200 MeV protons. The ratio of the cross-sections for tritium to argon-37 is 40 for 160 MeV protons, 15 for 1000 MeV protons and 20 for 6200 MeV protons. In some iron targets the radioactive isotope argon-39 was also measured [2]. The ratio of the argon-37 to argon-39 cross-sections is 0.8 and is independent of the proton energy. There are also measurements [3, 4] of tritium production by energetic protons in other target materials, such as aluminium, copper, and lead; however, the radioactive isotope argon-37 was not measured in these targets.

### Tritium in meteorites

Tritium was measured [5, 6, 7, 8, 9] in samples of about twenty different meteorites; tritium and argon-39 were measured simultaneously in samples of ten meteorites [10, 11]. In only two meteorites, Hamlet, a stony meteorite, and Aroos, a metallic meteorite, was the isotope argon-37 measured [11] in addition to the tritium and argon-39. In the Hamlet meteorite at the time of fall there were  $170 \pm 20$  tritium decays  $\text{kg}^{-1}\text{min}^{-1}$ ;  $13.5 \pm 2$  argon-37 decays  $\text{kg}^{-1}\text{min}^{-1}$ ; and  $6.0 \pm 0.4$  argon-39 decays  $\text{kg}^{-1}\text{min}^{-1}$ . The ratio of the radioactivities  $\text{H}^3/\text{A}^{39}$  was  $29 \pm 6$ . In the Aroos meteorite at the time of fall there were  $36 \pm 7$  tritium decays  $\text{kg}^{-1}\text{min}^{-1}$ ;  $22 \pm 6$  argon-37 decays  $\text{kg}^{-1}\text{min}^{-1}$ ; and  $16 \pm 2$  argon-39 decays  $\text{kg}^{-1}\text{min}^{-1}$ . The ratio of the radioactivities  $\text{H}^3/\text{A}^{39}$  was  $2.2 \pm 0.5$ .

This paper reports the first measurement [12] of tritium, argon-37 and argon-39 in the Bruderheim meteorite [13]\* a stony meteorite of the bronzite-olivine chondrite type. This meteorite contains a total of 23.9% iron, nickel and

TABLE I  
TRITIUM, ARGON-37 AND ARGON-39 IN THE BRUDERHEIM CHONDRITIC  
METEORITE WHICH FELL ON 4 MARCH 1960

Material	Weight (g)	Decays $\text{kg}^{-1}\text{min}^{-1}$			Ratios of radioactivities	
		Tritium	Argon-37	Argon-39	$\text{H}^3/\text{A}^{39}$	$\text{A}^{37}/\text{A}^{39}$
Bulk	50	—	$23 \pm 4$	$11 \pm 2$	—	$2.1 \pm 0.4$
Bulk	40	$260 \pm 30$	—	$10 \pm 1$	$26 \pm 5$	—
Metallic phase	7.5	$90 \pm 20$	—	$36 \pm 6$	$2.5 \pm 0.5$	—
Stony phase	39	$290 \pm 30$	—	$4.8 \pm 0.6$	$60 \pm 10$	—

\* Prof. R. E. Folinsbee generously gave us a sample of Bruderheim.

cobalt [14]. The metallic phase of the Bruderheim meteorite was separated from the bulk material. The results for the bulk material and for the metallic phase are given in Table I. In the bulk material there are  $260 \pm 30$  tritium decays  $\text{kg}^{-1}\text{min}^{-1}$ ;  $23 \pm 4$  argon-37 decays  $\text{kg}^{-1}\text{min}^{-1}$ ; and  $10 \pm 1$  argon-39 decays  $\text{kg}^{-1}\text{min}^{-1}$ . In the metallic phase of the Bruderheim meteorite there are  $90 \pm 20$  tritium decays  $\text{kg}^{-1}\text{min}^{-1}$ ; and  $36 \pm 6$  argon-39 decays  $\text{kg}^{-1}\text{min}^{-1}$ . These values are approximately twice the values obtained for the metallic meteorite Aroos; however, the ratio of tritium to argon-39 is approximately the same in the two cases. Tritium is concentrated in the stone phase of the meteorite, since this material contains 290 tritium decays  $\text{kg}^{-1}\text{min}^{-1}$  while the metallic phase contains only 90 tritium decays  $\text{kg}^{-1}\text{min}^{-1}$ . The ratio of tritium to argon-39 in the metallic phase is lower than that observed in iron targets, indicating that some tritium diffuses out of the metallic phase, possible because of its high nickel content.

#### Tritium in recovered satellite material\*

Tritium and argon-37 were measured [15] in iron and in lead from the Discoverer XVII satellite and in iron from the Discoverer XVIII satellite. Discoverer XVII was launched at 20:42 UT on 12 November 1960 and was in orbit for 50 h. The apogee was 995 km, and the perigee was 185 km. A large solar flare occurred on 12 November 1960. Discoverer XVIII was launched at 20:20 UT on 7 December 1960 and was in orbit for 75 h. The apogee was 688 km, and the perigee was 232 km. Both satellites were in polar orbits.

The satellite results are given in Table II. The material consisted of a 1/4-in sheet of lead from Discoverer XVII, battery cases from the same location in both

TABLE II

#### TRITIUM AND ARGON-37 IN MATERIAL FROM THE SATELLITES DISCOVERER XVII (IN ORBIT FOR 50 h) AND DISCOVERER XVIII (IN ORBIT FOR 75 h)

Satellite	Material	Weight (g)	Decays $\text{kg}^{-1} \text{min}^{-1}$ *		Ratio of atoms	Production rate (atoms $\text{kg}^{-1} \text{min}^{-1}$ )	
			Tritium	Argon-37		H <sup>3</sup>	A <sup>37</sup>
XVII	Pb (sheet surface)	172	$163 \pm 2$	—	—	520 000	—
XVII	Pb sheet	125	$24.0 \pm 0.5$	—	—	77 000	—
XVII	Pb sheet	560	$7.5 \pm 0.2$	$\leq 0.05$	$\geq 20\,000$	24 000	$\leq 1.2$
XVII	Pb sheet	560	$7.5 \pm 0.3$	—	—	24 000	—
XVII	Fe battery case	167	$56 \pm 3$	$2.6 \pm 0.3$	$2,900 \pm 300$	177 000	$60 \pm 6$
XVIII	Fe battery case	117	$7.0 \pm 0.5$	—	—	15 000	—
—	Pb sheet	157	0.6	—	—	—	—
—	Fe battery case	153	0.6	—	—	—	—

\* Activity is corrected to the time of recovery.

satellites. Lead and a battery case that had not been flown in the satellite served as control samples. All the samples except the control samples contained measurable amounts of tritium. The highest tritium activity,  $163 \pm 2$  decays  $\text{kg}^{-1}\text{min}^{-1}$ , was measured in material scraped from the surface of Discoverer XVII lead sheet. This activity corresponds to a production rate of 520 000 T atoms per  $\text{kg}^{-1}\text{min}^{-1}$  averaged

\* Dr. H. Yagoda generously gave us the material.

over the 50 h. The tritium production rate in the metallic phase of the Bruderheim meteorite was  $90 \text{ T atoms kg}^{-1}\text{min}^{-1}$  averaged over the time of several tritium half-lives. The tritium content of an identical battery case from Discoverer XVIII was  $7.0 \pm 0.5 \text{ decays kg}^{-1}\text{min}^{-1}$ , which corresponds to a production rate of  $15\,000 \text{ T atoms kg}^{-1}\text{min}^{-1}$ . Even though this production rate is lower by a factor of 12 than the production rate in the Discoverer XVII battery case, it is still higher by a factor of twenty than the highest tritium activity measured in any meteorite. The tritium in the lead samples of Discoverer XVII depended on the depth and position of the sample in the shell reflecting different amounts of shielding. Although the tritium contents of the satellite materials were unusually high, the argon-37 contents were not high. The argon-37 could be measured easily only in the Discoverer XVII battery case; in all other samples the argon-37 activity was either at the limit of detectability or zero. The argon-37 activity in the Discoverer XVII battery case was  $2.6 \pm 0.3 \text{ decays kg}^{-1}\text{min}^{-1}$ , which corresponds to a production rate of  $60 \text{ argon-37 atoms kg}^{-1}\text{min}^{-1}$ . The argon-37 production rate in the Aroos iron meteorite was  $22 \text{ argon-37 atoms kg}^{-1}\text{min}^{-1}$ . This amount of argon-37 can be explained by cosmic ray and solar flare particle interactions in the satellite material.

Our interpretation of these results is that the solar flare contains tritium. Some tritium is trapped in a region about the earth and remains in this region for several weeks after the flare. This interpretation accounts for the excess tritium contents in the satellite material without a corresponding excess for other radioactive isotopes. Tritium measurements in additional satellites should determine the time that the tritium remains trapped and the extent of the trapping region.

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## DISCUSSION V

**F. Begemann** (Federal Republic of Germany): Why does Dr. Fireman consider it necessary to assume the presence of tritons in the cosmic radiation coming from the sun — in this case from the solar flare?

**E. Fireman** (United States of America): The amount of tritium is too large to be explained on the basis of nuclear reactions. There are  $10^9 \text{ particles/cm}^2$  from the flare. Many more low-energy protons in the flare would be needed for the tritium production in the lead. Therefore tritium is present in the flare.

There is another possibility, however, namely, that tritium is present in the Van Allen belt, because the satellite went to an altitude of 1000 km. This second inter-

pretation is supported by the fact that the Discoverer XVIII battery case contains tritium. A blank, unflown battery case did not contain tritium. It does not appear that the difference in tritium contents of the satellite can be explained without solar flare tritium.

**F. Begemann:** In that case I have one further comment. If iron and other elements, especially the heavy ones, are bombarded with alpha particles, a stripping reaction takes place. The resulting picture is rather peculiar in that the alpha particles do not appear to stop: a proton is removed but the remainder, which is the triton, moves on. This phenomenon, which has been exhaustively measured at California, might provide an explanation for the rather strong depth variation which you found in the tritium. Moreover, I think it much more likely that there is a good ratio of alpha particles to protons in the solar flares but that they do not contain any tritons. Nothing is known about the presence or absence of tritium in the sun and there is no way to test for it. On the other hand, an explanation of the tritium in terms of this alpha particle process would certainly yield the right magnitude of production and probably — although this is only a "guesstimate" — the right depth dependence as well.

**E. Fireman:** We considered this possibility very carefully. Of all the processes we investigated, alpha particle stripping came closest to explaining the effects, but it was not large enough because an alpha particle stripping cross-section of greater than half a barn would be required.

**F. Begemann:** Do you know the ratio of alpha particles to protons in this solar flare? I suppose that at the altitude in question not much is known about it.

**E. Fireman:** I assume an impingement of  $10^9$  alpha particles or that the flare is all alphas.

**F. Begemann:** What is your estimate of  $10^9$  alpha particles based on?

**E. Fireman:** They are based on Van Allen's measurements, which were done with Explorer VII.

**F. Begemann:** But not during this particular flare?

**E. Fireman:** Yes, they were. As luck would have it, a switch that Van Allen had installed on Explorer No. VII to make his counters turn off after a certain period failed to work. Explorer No. VII served as a continuous monitor of the flare. Van Allen measured  $1-2 \times 10^9$  particles from the flare and that is the value I used in these calculations.

**H. von Buttlar (Federal Republic of Germany):** What were the results of the bismuth-205 measurements you mentioned?

**E. Fireman:** The measurements at both Chicago and Brookhaven agreed well, indicating the presence of  $10^7$  low-energy protons in the energy range where the protons changed the lead to bismuth-205. The bismuth could be cited as a further argument against the alpha stripping process, because in the stripping the lead goes to bismuth-205 and the bismuth-205 is too small compared to the tritium.

**D. Lal (India):** I have a comment on the interesting paper and observations of Dr. Fireman. Mention has been made of the possibility that tritium is present in the Van Allen belt. I would like to draw attention to the results obtained by Friden and White who measured the energy spectrum and composition of particles in the belt, including the abundance of tritium, i. e. the ratio of tritium to protons. As far as I can see, these measurements cannot explain the tritium as due to incident tritons stopping.

**E. Fireman:** I would say their energy range is different from ours. I think they start from about 120-200 MeV tritons.

D. Lal: That is true. Their energy spectrum is very steep, having a differential slope of 4.5. Approximately 100 MeV tritons are required for penetration. Assuming that the tritium is there, the abundance is very small and it is simply impossible to reach a point where high tritium levels can be measured.

The requirement of half a barn, as Dr. Fireman has pointed out, is very subjective. As far as I know, no measurement of total proton flux was made in the case of this particular solar flare, in which much more intense production of protons from the sun would have been possible. I quite agree with Dr. Begemann that a considerable amount of tritium could be produced from heavier elements by a stripping reaction if they were accelerated during the flares. If, as I think, production of the tritium is connected with the solar flares, the depth dependence observed for the tritium concentration by Dr. Fireman can probably be satisfactorily explained if it is assumed that most of the tritium found is produced by low energy protons having a differential spectrum of the form  $E^{-4}$  or  $E^{-5}$ , as measured for solar flare protons. Offhand, I do not think there is going to be any serious difficulty with this. However, I see no justification for assuming that a flux of tritons from outer space impinged upon the battery, the more so since it is difficult to see how such a large percentage ( $\frac{T}{H} \sim 10^{-2}$ ) of the fast ( $\sim 100$  MeV) tritons required in such a case could be present in the flare-accelerated particles. Such an assumption is unjustified because most of the tritium which came from outside would, it seems to me, have to be produced in low energy nuclear reactions near the regions of acceleration and then the energy spectrum of tritons would be nearly terminated at about 15-20 MeV. The flux of higher energy tritons particles would be very small. I think the question is still open, but my personal opinion is that most of the tritium observed by Dr. Fireman in Discoverers XVII and XVIII is due to proton-induced reactions in flight.

E. Fireman: I would agree with you if the flux were one or two orders of magnitude larger than that measured by Van Allen. You may not fully agree with Van Allen's findings, but the fact remains that my conclusions are based on his estimates of the flux impinging on the satellite. If the figure is increased cross-section decreases proportionately.

D. Lal: Does Van Allen indicate any error or does he consider it an order-of-magnitude estimation?

E. Fireman: He gives a value of between  $1-2 \times 10^9$  particles per  $\text{cm}^2$ , and he prefers a figure of  $1 \times 10^9$ . My conclusions are based on that.



# TRITIUM STUDIES IN THE UNITED STATES GEOLOGICAL SURVEY

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## Abstract — Résumé — Аннотация — Resumen

**Tritium studies in the United States Geological Survey.** The Geological Survey is conducting a programme of research in laboratory analysis of tritium and in several field projects designed to test the value of tritium in hydrologic research.

Laboratory studies have been undertaken to improve the gas-phase counting technique and to develop a simple instrumentation adapted to programme requirements of long-range hydrologic research. Investigation of various gas-counting mixtures indicates that hydrogen-ether and hydrogen-ethylene mixtures are superior.

Electrolytic enrichment has been investigated with the objective of improving reproductibility and evaluating separation factors under several conditions. A system that provides 75% tritium recovery on a routine basis has been developed.

The principal field projects consist in:

- (1) A tritium study in the Coastal Plain of New Jersey indicating that layering of water of different ages occurs beneath the water table;
- (2) Studies in two different geologic terranes for determination of the fate of tritium fallout in the 1958 thermonuclear bomb tests;
- (3) Use of tritium to determine ground-water recharge to Tertiary sandstones underlying the semi-arid High Plains of New Mexico;
- (4) A study of tritium content of the ground water of the Snake River Plain in Idaho to develop information on the age of and rates and direction of movement of water; and
- (5) Use of manufactured tritium as a tracer for determination of the capacity of an underground reservoir near Carlsbad, New Mexico.

**Le tritium dans les études entreprises par le Service géologique des Etats-unis.** Le Service géologique poursuit un programme de recherches qui comprend l'analyse du tritium au laboratoire et plusieurs projets exécutés sur le terrain et destinés à vérifier quelle est l'utilité du tritium dans la recherche hydrologique.

Il a entrepris des études de laboratoire pour améliorer la technique de comptage en phase gazeuse et mettre au point un appareillage simple, adapté aux besoins du programme en matière de recherches hydrologiques à long terme. L'étude de divers mélanges de gaz pour le comptage indique la supériorité des mélanges hydrogène-éther et hydrogène-éthylène.

Le Service a fait des recherches sur l'enrichissement électrolytique en vue d'améliorer la reproductibilité et d'évaluer les facteurs de séparation dans différentes conditions. Il a mis au point un système qui permet de récupérer régulièrement 75% de tritium.

Les principaux projets exécutés sur le terrain sont:

1. Une étude au moyen du tritium faite dans la plaine côtière du New Jersey, d'où il ressort qu'il se produit sous le niveau de la nappe aquifère une superposition par couches des eaux de différents âges.
2. Des études sur deux différents massifs autochtones, dont l'objet est de déterminer le sort des retombées de tritium provenant des essais de bombes thermonucléaires effectués en 1958.
3. L'utilisation du tritium en vue d'étudier le réapprovisionnement en eau souterraine des grès tertiaires qui constituent le soubassement des hauts plateaux semi-arides du Nouveau-Mexique.
4. Une étude sur la teneur en tritium des eaux souterraines de la Snake River Plain dans l'Idaho, dont l'objet est de recueillir des renseignements sur l'âge de ces eaux, ainsi que sur leur débit et la direction de leur mouvement.
5. L'utilisation comme indicateur de tritium préparé, en vue de déterminer la capacité d'un réservoir souterrain près de Carlsbad (Nouveau-Mexique).

**Изучение трития в связи с геологическим обследованием сша.** Управление геологического обследования проводит исследовательскую программу как по линии лабораторного анализа трития, так и в целом ряде проектов на местах, направленных на изучение возможной фоли трития в гидрологических изысканиях.

Лабораторные исследования были предприняты с целью усовершенствования техники отсчетов импульсов газовой фазы, а также с целью разработки простых приборов, приспособленных для выполнения программы долгосрочного гидрологического обследования. Изучение различных пригодных для счета газовых смесей показывает на преимущества смесей водорода с эфиром и водорода с этиленом.

Было изучено электролитическое обогащение с целью улучшения воспроизводимости и оценки коэффициентов отделения в разнообразных условиях. Была выработана система, обеспечивающая при обычной работе 75-процентное восстановление трития.

Главные проекты на местах представляются в следующем виде:

1) Исследование при помощи трития прибрежной долины Нью-Джерси показывает, что ниже горизонта грунтовых вод происходит расслоение воды в зависимости от ее возраста.

2) В двух различных геологических грунтах были произведены исследования для определения судьбы радиоактивных осадков трития после испытания термоядерной бомбы в 1958 году.

3) Тритий используется для определения восстановления водных апасов в третичных песчаниках подпочвенных пластов полупустынных лоскогорий Новой Мексики.

4) Производится исследование содержания трития в подпочвенных водах долины реки Снейк в Айдахо для получения сведений относительно возраста этой воды, скорости ее течения и его направления.

5) Искусственный тритий используется в виде индикатора для определения емкости подпочвенного водоносного бассейна вблизи Карлсбада, в Новой Мексике.

**El tritio en los estudios del Servicio Geológico de los Estados Unidos.** El Servicio Geológico de los Estados Unidos está llevando a la práctica un programa de investigaciones que abarca análisis de tritio en el laboratorio y varios estudios en el terreno, con el fin de probar la utilidad del tritio en las investigaciones hidrológicas.

Se han emprendido estudios de laboratorio tendientes a mejorar la técnica de recuento en fase gaseosa y a perfeccionar un instrumental sencillo que satisfaga las exigencias de un programa de investigaciones hidrológicas a largo plazo. De los estudios efectuados con distintas mezclas gaseosas de recuento, se deduce que la de hidrógeno-éter y la de hidrógeno-etileno son las más satisfactorias.

Se ha estudiado el enriquecimiento electrolítico con el propósito de mejorar la reproductibilidad del método y de evaluar los factores de separación en diferentes condiciones experimentales. Se ha encontrado un procedimiento que permite recuperar regularmente el 75 por ciento del tritio.

Los principales trabajos efectuados en el terreno consisten en:

1. Un estudio realizado con ayuda de tritio en la llanura costera de Nueva Jersey, el cual indica que debajo del nivel freático el agua aparece dispuesta en capas de diferentes edades.

2. Estudios en dos macizos autóctonos diferentes con el fin de determinar el comportamiento del tritio precipitado a raíz de los ensayos termonucleares realizados en 1958.

3. Utilización del tritio para determinar la renovación del agua subterránea en las areniscas terciarias subyacentes a los altiplanos semiáridos de Nuevo México.

4. Un estudio del contenido de tritio en las aguas subterráneas de la llanura del Snake River en Idaho, que se lleva a cabo en procura de datos sobre la edad, los caudales y la dirección de circulación del agua.

5. La determinación de la capacidad de un depósito subterráneo próximo a Carlsbad, Nuevo México, usando tritio industrial como indicador.

### 1. Tritium measurement research

At an early stage in the tritium hydrology studies of the United States Geological Survey it became apparent that the tritium-measurement procedures then in use were not ideal for hydrologic programmes involving several hundred samples a year. Cost was excessive, and the analytical conditions were too critical for routine use by technicians. Research in gas-phase counting of tritium and in a preparatory enrichment was undertaken by the junior author and is reported in detail elsewhere [1]. A generalized review of the results is presented here.

The gas-phase counting research involved mixtures of hydrogen with ammonia, ethers, ethylene, propylene and several other hydrocarbons, the structures of which indicated some ability to quench the Geiger discharge and prevent the formation of multiple pulses. While several gases exhibited quenching effects, the best combination of properties was obtained with hydrogen-ethylene and hydrogen-ether mixtures. Both give satisfactory plateaux of 100 to 200 V (depending on hydrogen pressure), and both have been used routinely at hydrogen pressures up to 50 cm. With dimethyl ether successful tritium counting has been conducted at 2 atm of hydrogen. Standard counting conditions in the Geological Survey laboratory are 40 to 50 cm of hydrogen with 6 cm of ethylene or 3 cm of ether. Pulses of several tenths of a volt are obtained across a 10- to 20-M $\Omega$  resistor. This permits the use of the relatively simple Geiger counting electronics with the advantages of insensitivity to small voltage fluctuation, favourable noise rejection, and reduced sensitivity to trace impurities (vapour from plastic seals, for example) in the gas mixture.

TABLE I

#### THE EFFECT OF TEMPERATURE AND ELECTROLYSIS ON TRITIUM RECOVERY

Temperature	Applied Voltage	Average Current (amp)	Recovery (%)
8°	2.6	1	83
25°	2.6	1	73
8°	3.1	3	58
25°	3.1	4	48

(The electrolyses were made in 40 ml glass cells with cylindrical nickel-iron electrodes. Average volume reduction from 10 ml to 0.6 ml.)

A relatively simple vacuum line for the conversion of the enriched sample to gas was designed to take advantage of the simplification permitted by the gas mixture. In this system the water vapour is drawn over hot zinc to produce hydrogen, which is adsorbed in a charcoal trap at liquid air temperature to maintain vacuum. On completion of reduction, the counter tube is filled with the required amount of quench gas, and the hydrogen is then released from the charcoal (by warming) and is introduced into the counter tube through an evacuated chamber. Because of the difference in molecular mobility, the quench gas in the counter tube is not taken up by the charcoal during the short exposure time involved.

Electrolysis research involved a study of parameters that affect the percentage of tritium recovery and its reproducibility. In general, the rate of heat transfer and the current density were the most significant factors. Adequate cooling of the cells is essential, because a local rise of temperature seriously reduces the tritium

recovery. In the Geological Survey laboratory the electrolyses are conducted in a two-stage system, using 500-ml iron cells for the first stage and 40-ml glass cells for the second stage. Recovery averages 90% in the iron cells and 85% in the glass cells, giving an over-all recovery of approximately 75 ( $\pm 5$ )%. The nickel-iron electrode combination is used. Oxidation of the iron seems to affect recovery adversely, and the cells are treated with acid between each run to remove any oxide film that may be present. Details of cell construction are given elsewhere [1]. Table I reports some typical results, obtained in electrolysis research, which show the effect of current density and temperature variation.

## 2. Tritium rainout study, 1958

Tritium produced by the 1958 thermonuclear-test series provided a useful label for studying the movement of atmospheric moisture from the Pacific Ocean and its distribution across the United States. The fate of this tritium cloud was observed by means of samples from a chain of collection stations operated by the United States Weather Bureau. Precipitation samples were collected at 12 stations, extending in a northwestern arc from San Juan, Puerto Rico, to Anchorage, Alaska. The sampling period was from early April to late July at most sites, with incomplete coverage at some. Generally, two-week integrated samples were collected, and these were analyzed for their tritium activity in the Geological Survey laboratory. Fission products were not measured. Only the major conclusions from this study are presented here, because the detailed data are presented in a paper by the junior author [2].

The average tritium concentrations in rainfall for the three to four month period at the 12 sampling stations are given in Table II. Contributions from individual

TABLE II  
AVERAGE TRITIUM CONCENTRATIONS IN RAINFALL OVER THE UNITED STATES, APRIL-JULY 1958

Location	Average Tritium Concentration (T/10 <sup>18</sup> H)	Chloride Concentration (mg/l)
San Juan, Puerto Rico	72	
Key West, Florida	81	4
New Orleans, Louisiana	107	0.8
Memphis, Tennessee	260	0.4
Milwaukee, Wisconsin	588	0.2
North Omaha, Nebraska	443	0.1
Salt Lake City, Utah	255	
Cheyenne, Wyoming	394	0.15
Medford, Oregon	283	0.3
Seattle, Washington	175	2
Juneau, Alaska	307	
Anchorage, Alaska	607	

(JUNGE and WERBY 1955-56: chloride data for the same sites, interpolated between isochlors, is shown for comparison.)

rains are weighted according to the amount of precipitation. Tritium concentrations were notably high in the continental interior of the United States in comparison with the low values in the coastal and marine areas. A plateau of tritium activity with an average of 475 T.U. extended across the central United States

from Cheyenne, Wyoming, to Milwaukee, Wisconsin. The average for the three coastal sites of New Orleans, Key West and Seattle was 121 T.U.; and the value for the single marine site (San Juan) was 72 T.U. The observed diluting effect of oceanic moisture on the coastal tritium rainout was the major observed geographical effect. No clear-cut latitudinal effect was found although, in general, precipitation at northern sites showed a higher average tritium activity than did precipitation at southern sites. However, the high value of 607 T.U. at Anchorage does not seem to be representative, because most of this activity was contributed during one period of two weeks, 16 to 29 July, when rainfall was disproportionately high. If the apparently abnormal period is disregarded, the average for Anchorage is only 247 T.U., close to the Juneau average of 307.

Dilution of tritium in coastal and marine atmospheric moisture masses, which was observed in this study, has a counterpart in the chloride-distribution data obtained by JUNG *et al.* [3] in their study of salt rainout over the United States from July 1955 to July 1956. They found chloride rainout in coastal areas ranging from approximately 1 mg/l to 6 mg/l, which dropped off rapidly in the interior to an average concentration of less than 0.2 mg/l. The tritium data and the chloride data seem to show general agreement on the extent of marine air-mass influence. Concentrations change rapidly — increasing for tritium and decreasing for chloride — in areas extending 300 to 500 miles inland, where a central plateau of more uniform values than those in coastal areas prevails. Estimated chloride-concentration values obtained from JUNG *et al.* data are given for the tritium-sampling sites in Table II. It was necessary to interpolate between isochlors in some cases because the two sampling sites did not coincide.

Although the tritium-sample collection programme did not extend long enough to define the decay side of the 1958 rainout, the data seem to indicate a tritium-concentration peak in late May and June for the mid-latitude areas of the United States and a July peak at the two Alaskan sampling sites.

### 3. The field tritium research programme

The field research programme of the Geological Survey was designed to test the value of tritium as a hydrologic tool, principally in ground-water studies. Because of its generally very slow movement, most ground water is older than the three to four half-lives of tritium through which tritium is detectable by laboratory analysis. For that reason the field research projects were limited to shallow water-table environments and to aquifers with very high permeabilities and rapid rates of ground-water movement. In such hydrologic environments the water is sufficiently young to contain detectable amounts of tritium or even to contain bomb tritium recharged since 1954. Three of the field research projects were specially designed to take advantage of recharge-containing bomb tritium from the United States and Soviet test series of 1958.

Two field projects were located in the Coastal Plain of New Jersey in areas underlain with highly permeable fine- to coarse-grained sand. One project in New Jersey involved a study of the tritium content of ground water at varying depths down to 100 ft below the water table in an observation-well field adjacent to the Mullica River. It was found that the ground water was layered in the order of age of recharge, with ground water just below the water table containing 1958 bomb tritium. Below the 1958 layer of recharge there was a progressive decrease in bomb tritium to a depth of more than 15 m, where the base of the 1954 recharge was found. Below 30 m the water contained no detectable tritium and was at least

25 years old. By comparison of the tritium content of the ground water with that of the Mullica River at several periods of base flow it was established that virtually all the ground-water discharge into the stream entered laterally from its bank and from just below the water table. This discovery supports the deduction that streams which drain horizontally-bedded sediments receive most of their base-flow drainage from those beds lying above the bottom of the stream. This is because permeability parallel to bedding almost always is far greater than cross-bed permeability.

During the period March through July 1958 the response of hydrologic systems to influx of new bomb tritium was studied at a second site in the New Jersey Coastal Plain and at a site near Madison, Wisconsin. Bi-weekly samples of precipitation runoff and ground water were analyzed for tritium content. Water and tritium budgets for the two basins during the period of observation are being prepared. The studies are leading to new information on how recharge moves through the vadose-water zone, through the ground-water reservoir and into streams. Information on the circulation of bomb tritium in the continental hydrologic cycle also is being obtained.

At a field project in the High Plains of New Mexico tritium analyses of ground waters for determination of their places of recharge have been made. The High Plains are dotted with numerous depressions in which water from precipitation collects and stands for varying periods of time. The depressions may not be the major intakes of recharge which they commonly are considered to be because of silting that takes place in the bottoms of the depressions. If the depressions are intakes of recharge, the ground water near them should generally be higher in tritium content and younger than ground water in areas well removed from the depressions.

Tritium analyses of ground water in the Snake River Plain of Idaho are being used in an attempt to determine the age, velocity and directions of flow of ground water in the basalt. Here the ground water flows through basalt that is remarkably permeable. The water travels through inter-bed zones at an average rate estimated to be on the order of 20 ft per day.

During the spring of 1961 the Geological Survey will conduct a tracer study with tritiated water as a label. The tracer-test site is at Lake McMillan, a shallow reservoir on the Pecos River near Carlsbad, New Mexico. A large amount of water leaks through the floor of the lake into an underground reservoir, which consists principally of gypsiferous limestone with solution channels developed in the limestone. Water from the underground reservoir discharges from springs in the Pecos River channel about three miles downstream from the lake.

The amount of tritiated water released to the reservoir will be adjusted to raise the level of the water to about 2000 T.U. Movement of the tracer front through the underground reservoir and out of the springs will be traced by sampling the springs and observation wells between the springs and the lake. Movement of the tracer through the hydrologic systems and other data will be used to estimate the volume of water in the underground reservoir and the rate of movement of the tracer through the system. This study is supported in part by the Office of Isotopes Development, United States Atomic Energy Commission.

In addition, a number of small-scale studies have involved the use of tritium as a hydrologic tool. For example, a field problem in the Arkansas and Red River basins of Oklahoma involved the source of salt-water springs — whether the water rose through fractures and faults from deep sources or was ground water that was recharged locally and became salty by passing through shallow halite-bearing rocks.

Field hydrologic studies indicated that the second hypothesis was the correct one. Tritium analyses showed that the water is young, confirming that, inasmuch as the water was shown to be young, it is of recent recharge origin.

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## DISCUSSION VI

**H. von Buttlar** (Federal Republic of Germany): With reference to Table I of Mr. Thatcher's paper and his measurement of the tritium recovery as a function of the current density, I must say that my experience has been just the opposite, i. e. the higher the current density, the higher the enrichment factor in electrolysis. I wonder whether these are his only measurements of this type or whether he has checked in more detail.

**L. Thatcher** (United States of America): We have other measurements on the recovery in electrolysis, but with our particular apparatus it does appear that the increase in current density reduces the tritium recovery. I think that is a matter of heat transfer, i. e. that we get local heating when we increase the current density. It is actually the rise in temperature that reduces the tritium recovery. This study is still in the empirical stage and the basic factors affecting the tritium recovery have not yet been clearly analyzed. However, I believe that the conditions can vary from apparatus to apparatus: i. e. it is quite possible to have improved recovery under high current density with one particular electrolysis unit and the opposite with another.

**E. Simpson** (United States of America): Could Mr. Thatcher tell us whether, in the New Jersey study, he has been able to compute a residence time for the various levels of ground water.

**L. Thatcher**: That will be calculated in due course. The data for this particular project is still being analyzed and the general hydrologic study will probably not be completed for another six or eight months.





# APPLICATION OF TRITIUM TRACER TO CANAL SEEPAGE MEASUREMENTS

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## Abstract — Résumé — Аннотация — Resumen

**Application of tritium tracer to canal seepage measurements.** The paper considers the problem of seepage loss from water carrier and storage systems and the application of tritiated water to the detection and measurement of such losses. A field study of seepage loss from an 800 ft reach of the Madera Canal, located in the San Joaquin Valley of California, was made. Tritiated water was employed to measure the progress of underground seepage from the canal and the loss of water from an isolated reach of the canal. Velocities of ground water flow were also determined by the point-dilution technique with both chloride and tritium tracers.

Laboratory studies of the point-dilution method were conducted for determination of its theoretical validity under controlled conditions and for comparison of the relative efficacies of chloride and tritium.

**Emploi du tritium comme indicateur pour mesurer les infiltrations dans les canaux.** Les auteurs examinent le problème des pertes par infiltration qui se produisent dans les réseaux de distribution et les réservoirs d'eau, ainsi que l'emploi d'eau tritiée pour déceler et mesurer ces pertes. Ils ont procédé à une étude des pertes par infiltration qui se produisent dans un tronçon de 800 pieds du canal Madera, situé dans la vallée de San Joaquin en Californie. Ils ont utilisé de l'eau tritiée pour mesurer les progrès des infiltrations souterraines d'eau provenant du canal et déterminer les pertes d'eau dans un tronçon donné du canal. Ils ont eu recours à la méthode de la dilution à partir d'un point et ont utilisé à la fois le chlorure et le tritium comme indicateurs.

Cette méthode de dilution a fait l'objet d'études au laboratoire en vue de déterminer dans quelle mesure elle est théoriquement valable dans des conditions déterminées et quelle est l'efficacité relative du chlorure et du tritium.

**Применение трития в качестве индикатора для измерения утечки в канале.** В докладе рассматривается проблема утечки воды из внутренних водных путей, из водохранилищ и применения тритированной воды для обнаружения и измерения такой утечки. Было проведено исследование на месте утечки воды из колена длиной в 800 футов на канале Мадера, расположенном в долине реки Сан-Хоакин в Калифорнии. Тритированная вода была использована для измерения хода подпочвенной утечки из канала и уменьшения воды в изолированном колене канала. Были также определены скорости подпочвенного течения точечным методом растворения (point-dilution) с использованием индикаторов в виде хлорида, и трития.

Было проведено лабораторное исследование этого метода для определения его теоретической правильности в контролируемых условиях и для сравнения относительной эффективности хлорида и трития.

**Empleo del tritio como indicador para medir las infiltraciones en los canales.** Los autores examinaron el problema de las pérdidas por filtración en los sistemas de conducción y depósito de agua y del empleo del agua tritiada para el estudio y medición de tales pérdidas. Dan cuenta de un estudio de las pérdidas realizado en un tramo recto de 800 pies de largo del Canal de Madera, situado en el valle de San Joaquín, en California. Utilizaron agua tritiada para medir el progreso de la filtración subterránea desde el canal y las pérdidas de agua en un tramo aislado del mismo. También determinaron las velocidades de la corriente subterránea aplicando el método de la dilución a partir de un punto con ayuda de cloruro y tritio como indicadores.

Estudiaron en el laboratorio este método de dilución a fin de determinar su validez teórica en condiciones controladas y de comparar la utilidad relativa del cloruro y del tritio.

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Seepage from unlined water carrier and storage systems may result in serious water losses and often creates undesirable ponding and saturating conditions on adjacent lands. In devising economic remedial measures it is necessary to estimate the origin, magnitude, and direction of the seepage, in order that impervious linings may be applied only to the more permeable portions of the structure. Areas suspected to be of high permeability can often be isolated through knowledge of soil conditions, by measurement of ground water levels, and by the appearance of springs or other hydrogeologic anomalies readily attributable to some nearby hydraulic structure. However, there are numerous situations where the origin and magnitude of seepage losses are not obvious and the necessity exists for more perceptive detection and measurement methodologies. It was for this reason that an investigation of tritium and other radioactive tracers was undertaken, with the expectation of developing practical methods of measurement to be employed as adjuncts to the more conventional approaches.

Seepage tracers can conceivably be employed in several ways. One approach is the addition of a gamma emitter to the canal water in a chemical state such that it will remain in solution or suspension, but will be filtered or sorbed by the soil materials in the areas of maximum leakage. A subsequent gamma survey of the canal walls and bottom would theoretically reveal the relative surface infiltration rates and thus the location of points of greatest seepage loss. A second technique is the addition of a soluble tracer that is not sorbed by the earth, but rather remains with the seepage water and may be detected by a suitable probe or sampling point located at some distance from the canal. By delineating the tracer concentration-arrival time function at the observation point, it becomes theoretically possible to estimate the flow velocity through the earth and thus also to estimate the canal seepage loss.

A third approach involves the placing of a water tracer in one or more test wells located near the canal and observing either the dilution of tracer from the test wells or the arrival of tracer at observation wells located downstream and in the suspected direction of ground water movement.

Although each of the above methods is theoretically workable and can provide meaningful results under the proper circumstances, each has certain practical limitations that restrict the range of practical application and may impair the accuracy under many circumstances encountered in the field.

Tritium in the form of tritiated water most nearly meets the criteria for the ideal ground water tracer in that it moves through all earth materials in a manner very nearly identical to that of ordinary "light" water. Its greatest advantage over other radioisotopes, and particularly those in the cationic form, is the absence of sorptive loss to the clays and other natural ion exchangers. Tritium holds a similar advantage over chemicals such as fluorescein and rhodamine-B, which are detectable in low concentrations and may be suitable tracers for surface waters, but are of questionable reliability in conducting ground water investigations.

The question of tritium adsorption is a matter of some interest, since tritiated water may move more slowly through a natural soil medium than the chloride ion and thus appear to be undergoing some form of adsorption. For example, in studies

of the passage of chloride and tritium through laboratory columns of Yolo sandy loam, chloride was observed to move at a velocity 1.22 times that of tritium [1]. In similar studies with a soil low in clay, the chloride-tritium velocity ratio was observed to be only 1.03 [1]. In these measurements it was believed that tritiated water molecules not only passed through the free pore water, but also exchanged with the water adsorbed on the clay minerals and the water of hydration of cations associated with these minerals. Thus, tritiated water can be expected to displace very nearly the entire water reservoir of a porous medium. Chloride, on the other hand, passes through only that portion of the water reservoir available to such an ion. A fair degree of correlation was observed to exist between the tritium-exchangeable water and the clay content of the material. This characteristic of the labelled water in no way impairs the utility of tritium, but rather represents one of its attributes. Expect under the most unusual circumstances, tritium loss by hydrogen ion exchange is negligible.

### Point-dilution method of velocity measurement

If a suitable radioactive or chemical tracer is introduced into a well perforated throughout its wetted depth, the natural motion of ground water will dilute the tracer at a rate proportional to the average water velocity along the aquifer profile intercepted by the well. If the aquifer is without vertical potential gradients and may be assumed to have a permeability very much less than that of the well, it can be shown that, theoretically, the well will intercept a portion of the ground water stream having a width equal to twice the well diam. Thus,

$$dc = -c \frac{8\bar{v}}{\pi d} dt, \quad (1)$$

and

$$c/c_0 = e^{-\frac{8\bar{v}}{\pi d} t}, \quad (2)$$

where  $d$  is the test well diam. and  $\bar{v}$  is the average macroscopic ground water velocity along the well profile. The average interstitial, or microscopic, velocity may be obtained by dividing  $\bar{v}$  by the fractional porosity,  $p$ .

The validity of equation (2) is dependent on the completeness of mixing within the test well relative to the rate of influx of dilution water, the relative mixing rate assuming greatest significance in formations having large inhomogeneities. However, the turbulence associated with mixing of the tracer should not cause excessive interchange between the water within the well casing and that in the adjacent formation. The coefficient  $8\bar{v}/\pi d$  may be evaluated by a semilog plot of relative tracer concentrations and a determination of the slope of the line of best fit.

There are numerous sources of error in the point-dilution method, and it can be expected to provide no more than an estimate of ground water velocities. For example, if the test well penetrates several strata at different hydrostatic potentials, the well serves as a low resistance channel, and vertical flow between the strata will occur, with a resulting increased rate of dilution and an erroneously high value for the ground water velocity. In driving the well casing into place an impermeable annulus may develop between the casing and the formation, and the observed velocity may be less than the true one. If the well is developed by surging to remove the compacted material, or if the hole is bored over-size, the effective well

diameter will be greater than  $d$ , and the observed velocity less than the true velocity. Similarly, in mixing the well water and in removing samples there is a tendency to cause the exchange of well water with formation water, with resulting high values of the observed velocity.

### Laboratory evaluation of the point-dilution technique

In order to test the validity of equation (2), an artificial gravity aquifer was prepared in a box constructed of wood and designed to allow the uniform horizontal flow of water. The flow length was 166.5 cm, with a width of 120.5 cm and an average wetted depth of 79.8 cm. The box was filled with sand to a depth of 100.0 cm, the sand having a 10% size of 0.28 mm, and a permeability of 0.02 cm/sec at unit gradient. A 10.0 cm diam. perforated pipe was located at the centre of the box and served as the test well. Both the chloride ion and tritiated water were introduced into the test well and their diminution with time measured under various flow rates through the box. Flow rates ranged from 12.3 to 106 ml/min. and corresponded to macroscopic velocities of 0.22 to 1.85 cm/h.

The relative tracer concentrations,  $c/c_0$ , were plotted against time on semilog paper, and  $\bar{v}$  was calculated from the slopes of the lines of best fit. These values have been plotted against the actual velocities computed from the measured flow rates and the known cross-sectional area of the artificial aquifer, and are shown on Fig. 1. The standard deviations of  $\bar{v}$  were estimated and are also shown. Agree-

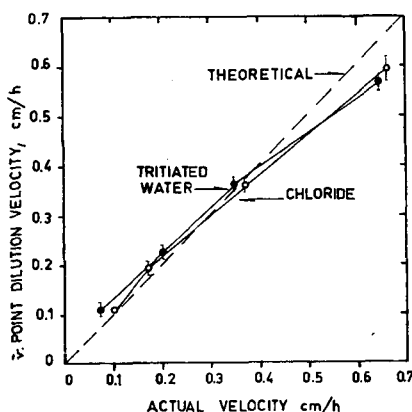


Fig. 1

Macroscopic velocity measurements by the point-dilution method.

ment with the theoretical relationship was quite satisfactory for the chloride tracer, and acceptable for the tritiated water. The tendency to overestimate velocities at low flow rates and to underestimate them at high rates is an expected one. With actual velocities approaching zero, diffusional mechanisms serve to transport tracer from the test well and thus give the appearance of a significant point-dilution velocity. At high velocities the test well has a greater likelihood of failing to meet the infinite permeability criterion, and the point-dilution velocity may appear to be less than the actual.

It is believed that Fig. 1 attests to the theoretical validity of equation (2), but also suggests certain practical limitations of the single-well velocity measurement technique.

### Deep-well application of the point-dilution technique

The single-well, or point-dilution, technique was also employed to estimate ground water velocities in a confined aquifer under investigation as part of waste injection studies, and in an unconfined aquifer adjacent to the Madera Canal. The latter study is described in a subsequent paragraph of this paper. The permeability of the confined aquifer ranged from  $4.0 \times 10^{-2}$  to  $8.9 \times 10^{-2}$  cm/sec, and was penetrated by 15 cm diam. test wells having depths of about 30 m. The 120 cm segment of casing penetrating the confined aquifer was isolated by a pair of rubber gaskets, and labelled water was circulated between this segment and the ground surface by a Sigma Motor pump (Fig. 2). This technique allowed the continuous,

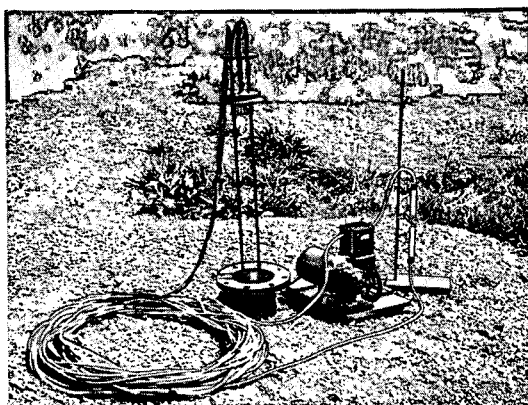


Fig. 2

Point-dilution equipment used in deep pressure well studies.

but gentle, mixing of the tracer in the test well and permitted periodic sampling at the surface. Uniformly consistent and reproducible results were obtained, with measured velocities in several wells ranging from 0.53 to 22.0 cm/h. Although accurate independent measurements of the actual ground water velocities were not possible, it is believed that the point-dilution velocities were within 25% of the true values as estimated from previously measured permeabilities and current piezometric gradients.

### Madera canal study

The Madera Canal is located on the east side of the San Joaquin Valley, California, in the foothills of the Sierra Nevada Mountains. It serves to transport irrigation waters from Friant Dam to the irrigation districts of Madera County. An 800 ft unlined section of the canal was selected for investigation and isolated with two plastic-faced earth dams. A typical cross-section of the canal and the topography in the expected direction of seepage loss are shown in Fig. 3. Test wells were dug with a mobile power auger and cased with 10 cm diam. perforated galvanized iron pipe. The location and designations of these wells are also shown in Fig. 3. Water was introduced into the test section on October 15, 1959, and was maintained at a nearly constant level until February 16, 1960.

The objectives of the Madera Canal field study were to examine two techniques of estimating canal seepage losses, the point-dilution method as previously de-

scribed, and the observation of tritium tracer arrival at the test wells, the tritium having been introduced into the canal impoundment. It was recognized that although both of these methods are theoretically sound when dealing with homogeneous systems of granular material, in the natural setting they both have obvious weakness that may well limit their practical utility. These limitations stem primarily from the inhomogeneities of natural formations and the great difficulty, if not the impossibility, of determining the location of such inhomogeneities and measuring their contribution to average flow rates. Thus, if a major fraction of

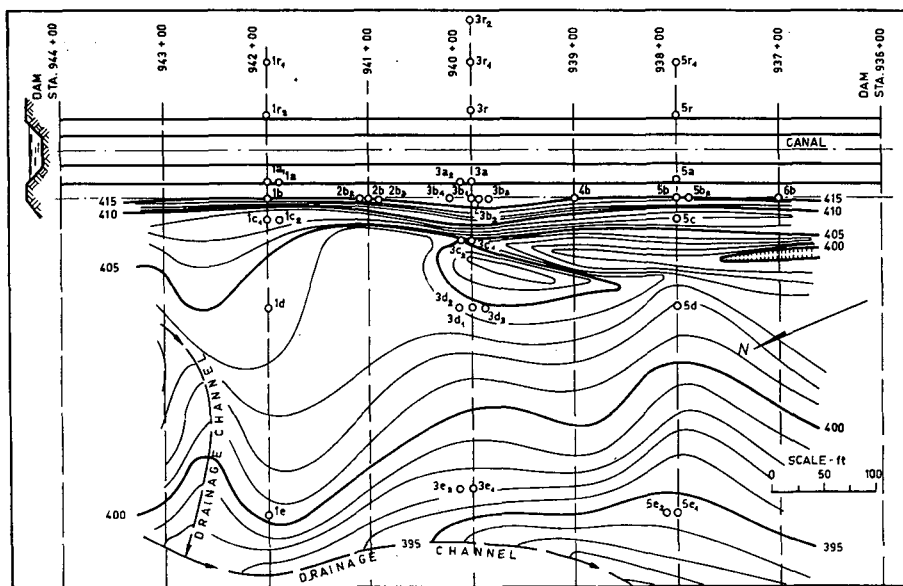


Fig. 3  
Seepage area, Madera Canal study.

the seepage loss occurs through stringers or lenticular regions of high permeability, but of limited areal extent, it is likely that both measurement systems would underestimate the average rate of transmission. Moreover, the point-dilution technique would tend to result in the lowest values, since a single 10 cm diam. well only samples the flow regimen in a vertical column approximately 20 cm in diameter.

The area chosen for the field test was believed to be reasonably homogeneous and one in which seepage losses were appreciable, as evidenced by ponding adjacent to the canal. A major fraction of the seepage loss was believed to occur through the west bank of the canal which was constructed of a light brown sandy silt containing little or no clay. Samples were removed from the test wells along the 1, 3, and 5 lines and classified as to texture on the basis of physical appearance. Generally, a 15 cm layer of dark brown clay was encountered at the surface. At progressively greater depths the profile materials ranged from sandy silt to silty sand to decomposing granite, but with great variations in relatively small distances. Fig. 4 illustrates the earth characteristics at the base of the west canal bank ("c" wells) and also shows the water levels prevalent during the test period. The parent material was obviously granite, the entire test area being underlaid at depths of 15 to 20 ft with a dense decomposing granite. It is probable that the zone of greatest

permeability was at the surface of the granite base, since gravelly sands and gravels were encountered in this region in the few test wells over 15 ft deep.

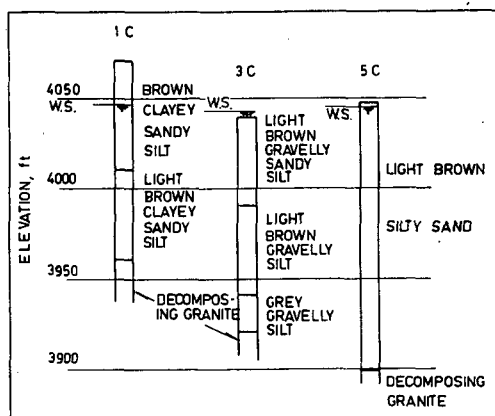


Fig. 4

Soil profiles, seepage area of the Madera Canal.

### Seepage measurements with tritiated water

On November 3, 1959, ten one-curie sources of tritiated water were introduced at equal intervals along the ponded canal at depths of about one meter. The tracer was mixed by motor boat for 75 min, and 23 samples of water were taken and analyzed for tritium. The average measured tritium concentration was  $1.48 \times 10^{-3} \mu\text{c/ml}$ , with a coefficient of variation of 10%. The concentration computed from the estimated canal volume of  $6710 \text{ m}^3$  was  $1.49 \times 10^{-3} \mu\text{c/ml}$ . The water level was maintained constant at Elev. 409.5 ft by the daily addition of water. These additions also permitted the computation of the rate of loss of water seepage. This rate decreased linearly from  $9000 \text{ ft}^3/\text{d}$  on November 3 to  $7000 \text{ ft}^3/\text{d}$  at 40 days. Early in the test period a leak developed beneath the north dam that fortunately remained quite constant at about  $1900 \text{ ft}^3/\text{d}$ , leaving a net bank seepage loss ranging from  $7100$  to  $5100 \text{ ft}^3/\text{d}$ . Records were maintained of the water levels in selected test wells, and these clearly indicated the major leakage loss to be through the west bank, as would be anticipated from the topography. However, it is quite possible that during the test period as much as 30% of the seepage loss occurred through the east bank.

Water samples were removed from the various test wells at sufficiently frequent intervals to delineate the passage of the tritium wave. Prior to sampling, each well was thoroughly mixed such that the tritium concentration was constant throughout the full depth. Samples removed from the *a*, *b*, and *c* wells during the first 30 days are the most meaningful for determining canal losses. However, a second interest was to obtain data on dispersion phenomena, and, consequently, the sampling program was continued for nearly 500 days and included observation points at distances of 350 ft from the canal. Fig. 5 shows the time progression of tritium concentrations in the No. 5 line of wells and is illustrative of the results obtained.

Theoretically, the time of tracer travel should be calculated from the time displacement of the centres of gravity of the concentration-time progressions for the canal and the observation wells. However, under the circumstances of this study, partic-

ularly considering the variable seepage rate and the dispersion of the tracer wave, the times of travel were estimated from peak tritium concentrations. From Fig. 5 it is readily evident that a low order of precision was inherent in these measurements

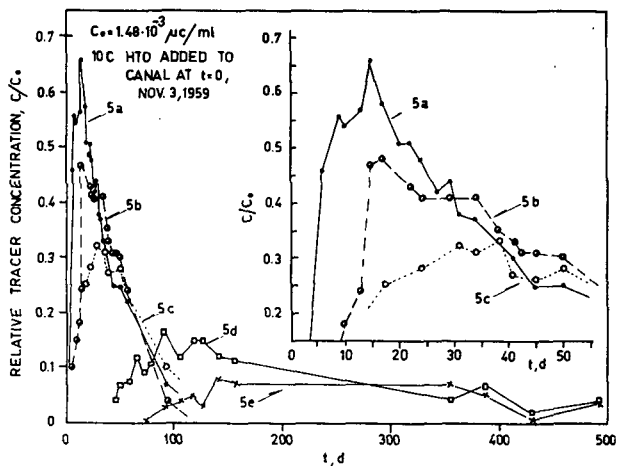


Fig. 5

Typical tritium-time progressions.

and in the velocities computed therefrom. A summary of the estimated average interstitial velocities based on tritium data from the *a* and *b* wells is shown in Table I. The macroscopic velocities may be obtained by multiplying the velocities in Table I by the fractional porosity, estimated at 0.35.

TABLE I  
INTERSTITIAL GROUND WATER VELOCITIES ESTIMATED FROM TRITIUM MOVEMENT DATA

Well	$\bar{v}/p$ ft/d	Well	$\bar{v}/p$ ft/d	Well	$\bar{v}/p$ ft/d
1a	0.70	3a	0.85	5a	1.1
1b	0.60	3b	0.75	5b	2.7

During the 20-day period of observation leading to the velocity data shown in Table I, the rate of seepage loss varied from 7100 to 6100 ft<sup>3</sup>/d. Assuming an average value of 6600 ft<sup>3</sup>/d and estimating the depth of flow from the water level profiles to be 10 ft at the *a* and *b* wells, the average macroscopic velocity was computed to be 0.83 ft/d. The corresponding average interstitial velocity would be 2.4 ft/d, or appreciably greater than the values reported in Table I. The average rate of seepage loss calculated from tritium arrival data taken at the nearest observation wells corresponded to 3000 ft<sup>3</sup>/d, whereas the actual loss rate was over twice this value, or 6600 ft<sup>3</sup>/d. It is evident that the observation wells, with perhaps the exception of 5 *b*, did not sample the seepage stream in a representative manner, and it is likely that a major portion of the seepage was taking place through lenticular irregularities of appreciably greater than average permeability. It is also quite possible that the seepage flow passed below the "*a*" line of wells, since these were located at the edge of the canal, 30 ft from the centreline, and only penetrated 4 to 6 ft below the canal bottom.



### Ground water velocities by the point-dilution method

A series of point-dilution velocity determinations was carried out on 13 selected wells over the period November 3—6, 1959. A second series of point-dilution measurements was carried on from January 26 through February 2, 1960. In both series of measurements a stock solution containing 1.12 meq/ml NaCl and 1.69 meq/ml  $\text{CaCl}_2$  was added in sufficient volume to raise the chloride content of the well, as defined by the casing, by 100 mg/l; and the rate of dilution was determined by periodic mixing, sampling, and chloride analysis. During the first series all casings were 10 cm in diameter, with four equally spaced 3 mm perforations at 10 cm intervals along the axis. Since the limited perforations were thought responsible for the low values of velocity determined in the first series of tests, the second series included five plastic casings of the same diameter, but perforated with four 3 mm  $\times$  13 cm slots at 15 cm intervals along the axis. Point-dilution measurements were also made at various depths in wells 2  $b_2$  and 3  $d_3$  by introducing a series of gaskets, or packers, that divided the wetted portion of the casing into five equal segments. Sigma Motor pumps were used to introduce and circulate the chloride tracer between each segment and the surface, thus permitting the taking of samples without removing the packers.

Point-dilution data, typical of the two series of tests, are shown in Fig. 6 for the

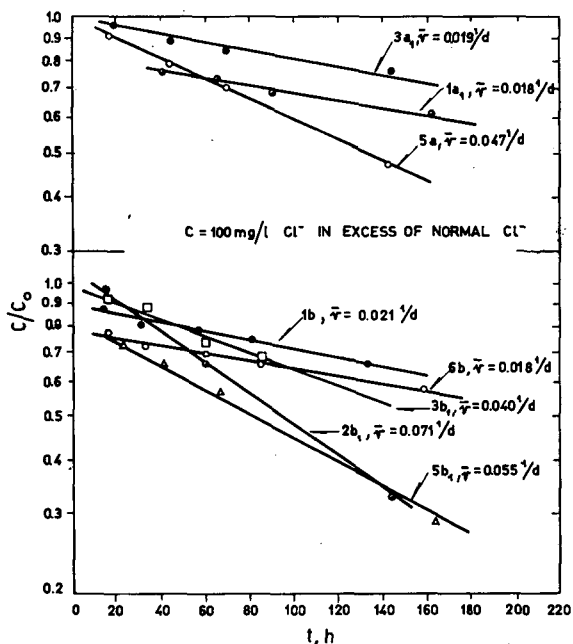


Fig. 6

Typical point-dilution data, Madera Canal study.

*a* and *b* wells. The individual interstitial velocities, as computed from equation (2) ( $p = 0.35$ ), are also shown. The data conform remarkably well to equation (2), as evidenced by the small departures of the individual points from the straight lines. However, conformity to the fact that the estimated average interstitial seepage

velocity on February 1 was approximately 1.0 ft/d\* is extremely poor. The point-dilution velocities in wells 5 *a* and 5 *b* were appreciably greater than those measured in the 1 *a*, 1 *b*, 3 *a*, and 3 *b* wells, a fact that bears some correlation with the data shown in Table I and with the soil profile data (Fig. 4). A comparison of the point-dilution results of the three wells, 3 *d*<sub>1</sub>, 3 *d*<sub>2</sub>, and 3 *d*<sub>3</sub>, provides some indication of the reliability of this method, as these wells were only 2 m apart. Well 3 *d*<sub>1</sub> was cased with perforated metal pipe and gave a velocity of 0.10 ft/d. Well 3 *d*<sub>2</sub> was constructed with slotted plastic pipe and gave a velocity of 0.20 ft/d. Well 3 *d*<sub>3</sub> was of plastic and was divided into five equal segments of about 60 cm each. The point-dilution velocities in the lower four segments were 0.25, 0.14, 0.12, and 0.15 ft/d, averaging 0.17 ft/d. It is apparent that point velocities varied appreciably over short distances, both vertically and horizontally. A comparison of the two types of casings at five locations revealed no significant differences in performance, even though the ratio of perforated areas was 34:1.

In summary, the interstitial point-dilution velocities ranged from 2 to 25% of that expected from the measured rate of water loss from the ponded canal. However, as mentioned previously, a majority of the sources of error can be expected to result in excessively great point-dilution velocities, rather than the underestimated values recorded in this study. From the laboratory studies and from the rather good correlation of the experimental data with equation (2), it must be concluded that the point-dilution method does provide a reasonably close estimate of the ground water velocity, but only in a relatively small region. In the case of seepage from the test section of the Madera Canal it is believed that a major portion of the loss occurred through permeable irregularities not penetrated by a majority of the test wells. It is also possible that the sandy gravel stratum located at depths greater than those penetrated by the test wells may have carried a major fraction of the water and thus contributed to the observed discrepancies.

### **Tritium as a ground water tracer**

Tritiated water is believed to be the only entirely satisfactory water tracer for problems involving flow through soils and earth materials. Thus, the failure to obtain reliable measures of ground water velocities in the canal seepage study is not attributable to the particular tracer, but rather to the inadequacy of the tracer methodology under the particular circumstances surrounding the study. If the canal were constructed in more homogeneous materials it is believed that more nearly correct velocities would have been measured by both the tritium travel method and by the point-dilution technique. The tracer could be introduced into the canal embankments as a step-function by simply feeding tritiated water into the canal at the head-works and maintaining a constant concentration of about  $10^{-4}$   $\mu\text{C}/\text{ml}$  for several hours. This procedure would allow for seepage measurement without interrupting the normal canal function.

It is well-known that the permeability characteristic of natural porous media is a highly variable quantity and is most practicably determined by test procedures involving large samples of the formation of interest. It is thus not unexpected to find groundwater velocities varying considerably from point to point, since these derive directly from local permeabilities and gradients. This relationship was borne out in the case of the point-dilution velocity measurements, whereas velocities determined from the passage of a tritium wave through 15 to 40 ft of formation were more consistent

\* Based on measured gross seepage loss rate of 4700 cu ft/d, less the leak in the north dam of 1900 cu ft/d.

and nearer the true average values. Additional experience with the techniques described herein will be necessary to ascertain their limits of applicability and the advantages to be derived from their employment as adjuncts to more conventional procedures.

### ACKNOWLEDGEMENTS

The authors are indebted to personnel of Region 2 of the Bureau of Reclamation, United States Department of the Interior, for their assistance in the conduct of the field tests. The authors are particularly grateful for the cooperation of Mr. Earl H. Bradley and Mr. Gordon Johnston of the Sacramento Regional office and Messrs. G. F. Hunter and G. D. Nielson of the Fresno office.

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### DISCUSSION VII

**D. B. Smith** (United Kingdom): Could Dr. Kaufmann say how long the tritium was kept in the canal? Did the concentration in the canal vary with time during the test? If it was steadily diluted by make-up water, what was the period required for dilution of the tracer by a factor of 2?

**W. J. Kaufman** (United States of America): We maintained the canal at constant level by the addition of water and consequently the tritium was diluted continuously throughout the study in an approximately exponential manner. This introduced a somewhat complicating mathematical equation when we attempted to determine the dispersion constants as the tracer passed through the adjacent ground materials. However, we made periodic measurements of the tritium concentration in the canal and this gave us a fourth measurement of the rate of loss from the canal which agreed quite well with the rate-of-loss measurement based on later changes in the canal water levels.

**W. F. Libby** (United States of America): Have you corrected for evaporative loss, or is that a minor matter?

**W. J. Kaufman**: No, we have not corrected for it, but we feel that, in the samples taken adjacent to the canal, the evaporative loss from the surface of the canal is relatively unimportant. We know that this was, at most, not more than about a few inches per month during the early part of the test period. However, in the samples taken further away, i. e. at distances up to 350 ft away from the canal, I feel that a good portion of the tritium was lost to the atmosphere by evaporation. We would have liked to measure it but we did not.

**H. G. Forsberg** (Sweden): Could Mr. Kaufman comment on the relative value of tritium and gamma-emitting nuclides as tracers for technical ground water studies and on the methods he used for taking samples and measuring tritium content in such work? It seems to me that, in suitable chemical form, gamma-emitters might be a very attractive means for investigating not only the velocity but also direction of escaping water where that was not known beforehand.

**W. J. Kaufman**: The problem in using gamma-emitters for ground water tracing is that most of the available ones — in fact all those that I know of — appear to be relatively unreliable or have relatively short half-lives (e. g.  $I^{131}$  and other

halides). They are also expensive. Their unreliability is due to sorptive loss on the soil clay. This applies particularly to the organic fraction of the material. In any event, we used only tritium in our study.

As to the second question, we used a liquid scintillation counter for our measurements, working with small, 20 ml vials and tritiated water samples of only 3.2 ml. We did not use the more sensitive systems available because our particular method was simpler and more economical.

**R. Wolf (France):** In normal operation, what are the velocities in the canal studied and what is the leak rate for the defective section?

**W. J. Kaufman:** The velocity in the canal during the time of the test was zero. The normal velocity in the canal is around 3—4 ft/sec. The ground water velocities that we measured were a few feet per day.

# THE ELECTROLYTIC ENRICHMENT OF TRITIUM AND DEUTERIUM FOR NATURAL TRITIUM MEASUREMENTS

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Abstract — Résumé — Аннотация — Resumen

**The electrolytic enrichment of tritium and deuterium for natural tritium measurements.** An electrolytic enrichment method is described, in which a 250 ml sample is electrolyzed in one cell to a final volume of 2.5 ml, or even less. In order to keep the electrolyte concentration within the tolerable limits, only a fraction of 50 ml of the sample takes part in the reaction, and by periodic addition in portions, the total sample is gradually introduced into the reaction zone. This method gives apparent enrichment factors for deuterium,  $\alpha'$ , and for tritium,  $\beta'$ , which vary according to the relationship

$$\eta' = \log \beta' / \log \alpha' = 1.369 \pm 0.006.$$

If this result is applied to conventional batch electrolysis the result may be written

$$\eta = \log \beta / \log \alpha = 1.337 \pm 0.007.$$

The experimental results, when furthermore corrected for vapour loss, are in excellent agreement with the prediction by Bigeleisen on theoretical grounds that  $\log \beta_0 / \log \alpha_0 = 1.40 \pm 0.01$ .

**L'enrichissement électrolytique du tritium et du deutérium en vue de la détermination quantitative du tritium naturel.** Les auteurs décrivent une méthode d'enrichissement électrolytique qui consiste à électrolyser dans une cellule unique un échantillon de 250 ml de manière à obtenir un volume final égal ou même inférieur à 2.5 ml. Afin de maintenir la concentration de l'électrolyte dans les limites admissibles, on n'introduit l'échantillon dans la zone de réaction que par fractions successives de 50 ml. Cette méthode permet d'obtenir les facteurs d'enrichissement apparent  $\alpha'$  pour le deutérium et  $\beta'$  pour le tritium, qui varient selon la relation:

$$\eta' = \log \beta' / \log \alpha' = 1,369 \pm 0,006.$$

Appliqué à l'électrolyse intermittente classique, ce résultat peut s'exprimer comme suit:

$$\eta = \log \beta / \log \alpha = 1,337 \pm 0,007.$$

Une fois corrigées pour tenir compte des pertes de vapeur, les données expérimentales concordent parfaitement avec les prévisions théoriques de Bigeleisen, selon lesquelles  $\log \beta_0 / \log \alpha_0 = 1,40 \pm 0.01$ .

**Электродитическое обогащение трития и дейтерия для измерений природного трития.** Дается описание метода электродитического обогащения, при котором 250 мл образца подвергаются электролизу в одном электролизере до окончательного объема в 2,5 мл или даже меньше. Для того, чтобы удержать концентрацию электролита в допустимых пределах, берется лишь 50 мл образца для участия в реакции, а весь образец постепенно вводится в зону реакции путем периодического добавления порциями. Этот метод дает истинные коэффициенты обогащения для дейтерия- $\alpha$  и для трития- $\beta$ , которые изменяются согласно формуле:

$$\eta' = \log \beta' / \log \alpha' = 1,369 \pm 0,006$$

Если этот результат применить к обычному периодическому электролизу, то итог можно выразить следующим образом:

$$\eta = \log \beta / \log \alpha = 1,337 \pm 0,007$$

Экспериментальные результаты с поправкой на испарение полностью согласуются с утверждением Бигелейзена, основанном на теоретическом предположении о том, что  $\log \beta_0 / \log \alpha_0 = 1,40 \pm 0,01$ .

**Enriquecimiento electrolítico del tritio y del deuterio con miras a la determinación cuantitativa del tritio natural.** Los autores describen un método de enriquecimiento electrolítico con arreglo al cual una muestra de 250 ml se somete a electrólisis en una celda hasta alcanzar un volumen final de 2,5 ml, o menor. Para mantener la concentración del electrolito dentro de los límites de tolerancia, sólo una fracción de 50 ml de la muestra participa en la reacción, en tanto que el resto de la misma se va introduciendo gradualmente en la zona de reacción por adición periódica de nuevas porciones. Este método permite obtener los factores de enriquecimiento aparente del deuterio,  $\alpha'$ , y del tritio,  $\beta'$ , que varían según la relación:

$$\eta' = \log \beta' / \log \alpha' = 1,369 \pm 0,006.$$

Si este resultado se aplica a la electrólisis intermitente clásica, el resultado puede expresarse de la manera siguiente:

$$\eta = \log \beta / \log \alpha = 1,337 \pm 0,007.$$

Una vez aplicada la corrección para tener en cuenta la pérdida de vapor, los resultados experimentales concuerdan muy bien con el valor  $1,40 \pm 0,01$  que predijo Bigeleisen para el cociente  $\log \beta_0 / \log \alpha_0$  basándose en consideraciones teóricas.

## Introduction

The fact that there are very low specific tritium activities in water of all kinds found in nature makes it necessary to enrich the tritium in most of the samples to be measured. This can be achieved by electrolysis of the water until only a very small fraction of the original volume, containing a large part of the initial tritium, remains. The electrolysis is performed in an alkaline solution. Experience has shown that the concentration of the hydroxide has to be between about 1 and 20%. High degrees of enrichment, i.e. with volume reduction factors between  $10^{-2}$  and  $10^{-5}$ , have been obtained by electrolysis in subsequent stages [1], a volume reduction of the order of  $10^{-1}$  being made in each of three to five stages. Between each stage the sample has to be distilled for reduction of the concentration of hydroxide.

The improved characteristics of our counting system [2], however, have made it possible to decrease the degree of enrichment necessary so that a volume reduction factor of  $10^{-2}$  is sufficient in nearly all cases, except for samples of sea water and other "old" waters. In addition, the design of our electrolysis cell makes it possible to reduce the initial sample volume of 250 ml to 2.5 ml in one cell, thus decreasing the amount of manual work to be spent on each sample and improving the accuracy by reducing the number of liquid transfers.

A knowledge of the relationship between the enrichment of deuterium and that of tritium is of the greatest importance for tritium measurements in unknown samples. KAUFMAN and LIBBY [1] have made such an investigation. Because of the presumed improvement in overall accuracy for our entire apparatus and the slightly different electrolyzing conditions, we decided to re-examine the enrichment problem, giving special consideration to experimental details.

### Fundamental formulae

Suppose we have a water sample of  $V$  ml containing  $n_P$  moles of protium,  $n_D$  moles of deuterium and  $n_T$  moles of tritium. During electrolysis these quantities can be regarded as fitting the following formula:

$$\frac{dn_P}{n_P} = \frac{\alpha dn_D}{n_D} = \frac{\beta dn_T}{n_T}. \quad (1)$$

Integrating this equation from the initial  $n_P^0$ ,  $n_D^0$  and  $n_T^0$  to the final condition, considering that  $n_P \gg n_D \gg n_T$ , assuming the molar volume of  $H_2O$  and  $D_2O$  to be equal, and using  $\alpha$  and  $\beta$  as the average values of these factors during the electrolysis, we get

$$\frac{V}{V_0} = \left[ \frac{n_D}{n_D^0} \right]^\alpha = \left[ \frac{n_T}{n_T^0} \right]^\beta. \quad (2)$$

By using  $X$ :  $s$  for the molar fractions of the isotopes in question, (2) can be transformed to:

$$X_T^0 = X_T \cdot \frac{V}{V_0} \left[ \frac{X_D^0 V_0}{X_D V} \right]^{\alpha/\beta}. \quad (3)$$

Equation (3) shows which quantities have to be known for determination of an unknown assay of tritium in sample of natural water. The reciprocal value of the exponent was determined by KAUFMAN and LIBBY [1] to be  $\beta/\alpha = 2.10 \pm 0.10$ . Now, because our experimental apparatus differs from theirs, it should be described before further deductions are made.

### Experimental procedure

The design of the electrolysis cell (given in Fig. 1) shows some resemblance to that of BROWN and GRUMMITT [3]. To provide a large electrode surface area within a small volume, the 34 cm<sup>2</sup> electrodes are located in a flattened glass tube with a volume of 25 ml when filled to the upper edge of the electrodes. The cross section C shows "channels" which have been designed to avoid implosion by evacuation; these channels also greatly aid convection of the liquid during electrolysis. The lowest, narrow part of the cell has a capacity of about 3 ml. The total volume up to an upper index mark is about 50 ml. As usual, iron and nickel are used respectively for the cathode and the anode and are kept in position by suitable indentations in the glass. The connecting leads support two "Teflon" baffle plates which trap droplets during electrolysis and the final distillation. A 250 ml drop funnel is mounted on the top of the cell.

Of a 250 ml sample, about 50 ml is charged into the cell, and about 0.6 g of sodium hydroxide is added. After immersion of the cell in a water bath up to slightly below the ground joint, the remaining portion of the sample is charged into the drop funnel. The water bath is kept at  $10.5 \pm 0.3^\circ\text{C}$  by a refrigeration unit, operated by a contact thermometer. This reduces the evaporation loss, which would lower the recovery yield of the heavy isotopes during the electrolysis. The electrolysis is made at 3.0 A (i. e.,  $0.09 \text{ A cm}^{-2}$ ) supplied by a constant current battery charger. The temperature of the liquid is never more than  $0.5^\circ$  higher than that of the cooling water. In 24 hours the volume decreases to about 25 ml; and by turning the stop-cock of the drop funnel a fresh portion of the samples is added up to the 50 ml index, and the electrolysis is continued. After eight days the drop funnel is empty, and after nine days the sample volume is 25 ml. When this volume remains, or at

the latest when a residue of 15 ml remains, the current is lowered to about 0.4 A, provided by another power supply. Within about six days the liquid level is down to the beginning of the narrowest part of the cell, the remaining water quantity being about 2.5 g; and the electrolysis is stopped.

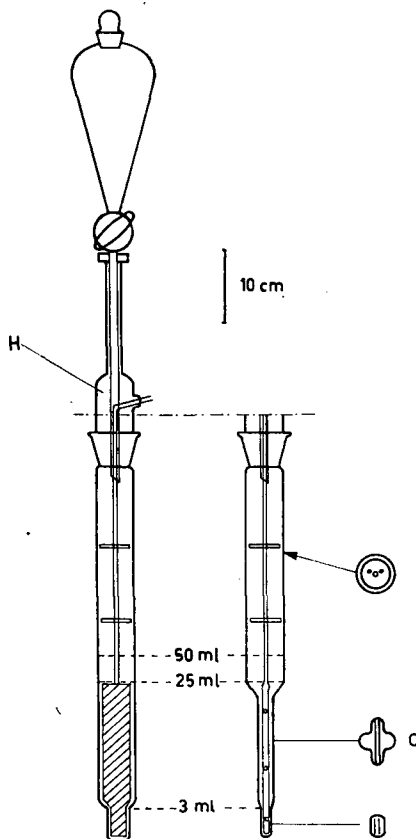


Fig. 1

Electrolysis cell for periodic addition.

To prevent large amounts of hydrogen from being bound in the NaOH, the enriched sample is neutralized with carbon dioxide to  $\text{Na}_2\text{CO}_3$  before distillation. This is arranged by removal of the head H (Fig. 1), introduction of a thin brass tubing reaching to the bottom, and bubbling carbon dioxide through the liquid at a fixed speed for a fixed time, determined by preliminary experiments. After neutralization, the cell is connected to a distillation head D (Fig. 2), carrying a Pirani gauge head P and a weighed receiving bottle B, kept at  $-80^\circ\text{C}$  by dry ice trichloroethylene. The system is cautiously evacuated while the water freezes out in the trap. The lower half of the electrolysis cell is heated gradually with an electric pad to about  $150^\circ\text{C}$ , and the distillation is performed at 2–5 mm Hg, taking about an hour. The final water volume V is determined by weighing the bottle before and after distillation. Careful checks have shown that this procedure yields  $99 \pm 1\%$  of the total hydrogen in the concentrate.



### Determination of the enrichment factors

In order to determine the enrichment factors, 14 solutions prepared from ordinary water, heavy water, and tritiated water were electrolyzed.  $V_0$  and  $V$  were obtained by weighing,  $X_D^0$  was calculated from the quantity of 99.9% heavy water used in

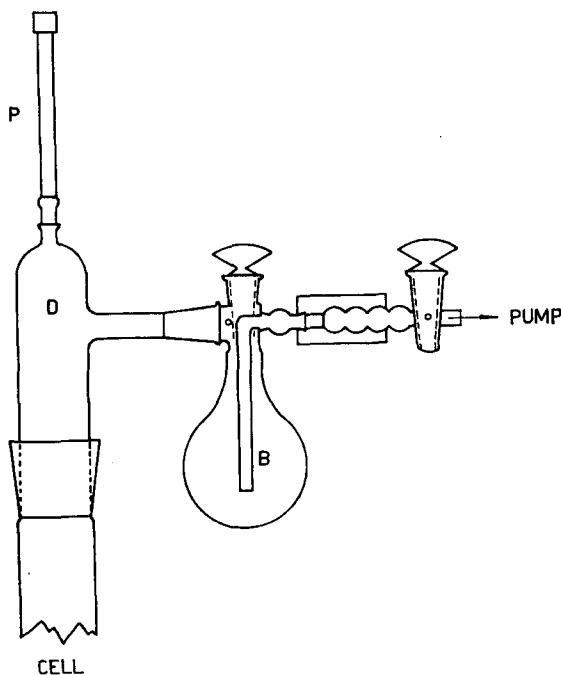


Fig. 2

Set-up for distillation of the enriched sample.

preparing the solution.  $X_D$  (and two  $X_D^0$ 's) was measured mass spectrometrically, and  $X_T^0$  and  $X_T$  were measured in our hydrogen counting apparatus [2]. Since our periodic addition procedure does not exactly fulfill the requirements given in the deductions of (2) and (3), the following formulae are used instead:

$$\frac{V}{V_0} = \left[ \frac{X_D V}{X_D^0 V_0} \right] \alpha' = \left[ \frac{X_T V}{X_T^0 V_0} \right] \beta' \quad (4)$$

$$\log \beta' / \log \alpha' = \eta'. \quad (5)$$

BIGEISEN's [4] theoretical result makes (5) more attractive than the ratio  $\beta'/\alpha'$  itself.

By denoting the recoveries of protium (volume), deuterium and tritium by  $R_V$ ,  $R_D$  and  $R_T$ , (4) is transformed to:

$$R_V = R_D \alpha' = R_T \beta'. \quad (6)$$

In Table I are given the results obtained with synthetic solutions. Fig. 3 shows strikingly the fact that  $\beta'/\alpha'$  is a function of  $\alpha'$ . The axes of each ellipse corresponds approximately to the rms errors of  $\alpha'$  and  $\beta'/\alpha'$  respectively.

It is convenient to evaluate a good empirical formula in terms of  $\beta'/\alpha'$  as a linear function of  $\alpha'$ . BIGEISEN's [4] investigation, however, suggests a constant ratio

TABLE I  
DETERMINATION OF THE APPARENT FRACTIONATION FACTORS

Run No.	$V_0$ ml	$V$ g	$X_D$ wt %	$X_D$ wt %	$X_T^0$ counts/min	$X_T$ counts/min	$\alpha'$	$\beta'$	$\beta'/\alpha'$	$\log \frac{\eta'}{\beta'/\log \alpha'}$
1	244.5	2.826	1.151	28.16	97.1	3913	3.53	5.84	1.65	1.399
2	244.5	2.596	1.165	37.45	102.2	4992	4.23	6.92	1.64	1.341
3	244.5	3.139	0.865	24.86	67.2	3012	4.37	7.88	1.80	1.400
4	244.5	4.272	0.839	18.29	74.9	2412	4.19	7.04	1.68	1.362
5	239.5	4.177	1.166	22.63	102.2	3018	3.74	6.10	1.63	1.371
6	248.0	4.731	0.168	5.50	10.80	456	8.41	18.31	2.18	1.365
7	239.5	2.563	1.166	38.38	101.8	5168	4.35	7.44	1.71	1.365
8	239.5	1.477	1.125	56.22	47.0	3763	4.32	7.15	1.65	1.344
9	229.5	1.208	0.705	35.92	50.9	4233	3.98	6.35	1.59	1.338
10	175.0	4.130	1.165	23.26	98.2	2816	4.98	9.59	1.93	1.408
11	250.0	4.313	1.165	21.30	149.4	4044	3.52	5.58	1.59	1.366
12	250.0	3.028	1.700	80.20	103.6	6622	7.89	16.68	2.12	1.362
13	250.0	3.101	1.700	76.07	103.6	6327	7.61	16.04	2.11	1.367
14	246.0	4.357	0.167	5.48	10.79	472	7.43	15.80	2.13	1.376

Average  $\log \beta'/\log \alpha' = 1.369 \pm 0.006$

of  $\log \beta'/\log \alpha'$ . This ratio has been calculated and the result applied to our periodic addition electrolysis. The function thus is best expressed by

$$\eta' = \log \beta'/\log \alpha' = 1.369 \pm 0.006. \quad (7)$$

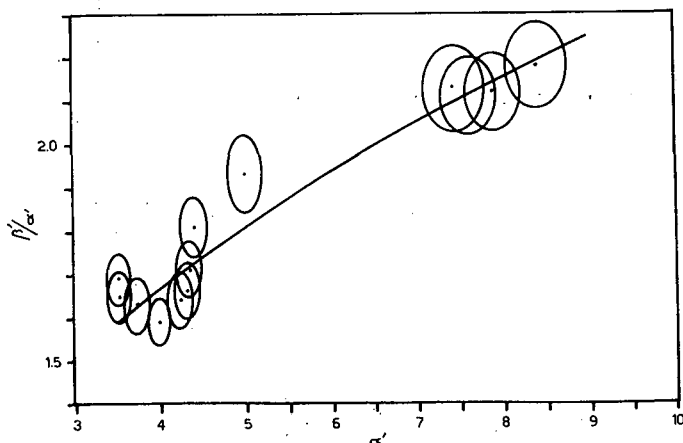


Fig.3

Variation of  $\beta'/\alpha'$  with  $\alpha'$ . The curve is drawn from  $\log \beta'/\log \alpha' = 1.369$ .

## Discussion

### (a) INFLUENCE OF THE PERIODIC ADDITIONS

Table I shows values of  $\eta'$  determined from the equations (4) and (5), using only the initial and final conditions of the sample. It is rather obvious, however, that our quantity  $\eta'$  differs somewhat from the value of  $\eta$  which should be obtained by electrolysis in the normal way, i. e. with the total sample taking part in the reaction during the entire course of the enrichment. The difference between these two cases can be calculated in the following manner.

Electrolysis is started with  $0.2 n_D^0$  and  $0.2 n_T^0$  in the reacting liquid, and  $\alpha$  and  $\beta$  are presumed to be constant during the entire procedure. At the end of the first day the remaining deuterium quantity is  $n_D^1$ .

$$n_D^1 = 0.2 \cdot n_D^0 \cdot A \text{ where } A = (1/2)^{1/\alpha}. \quad (8)$$

25 ml, i. e. another  $0.1 n_D^0$  moles of deuterium are added and this new total quantity of deuterium is reduced by a factor of  $A$  over night. At the end of the ninth day, 25 ml of the original 250 ml remains, and the recovery of deuterium is now

$$r_D = \frac{n_D^9}{n_D^0} = 0.2 A^9 + 0.1 \sum_{n=1}^8 A^n. \quad (9)$$

Electrolysis is now continued to the final volume of  $V$  ml, where the overall recoveries  $R_D$  and  $R_T$  of deuterium and tritium are obtained. The relationships between  $\alpha$ ,  $\alpha'$ , and  $\beta$ ,  $\beta'$  are given by

$$R_D = r_D (V/25)^{1/\alpha} = (V/250)^{1/\alpha'}, \quad (10)$$

$$R_T = r_T (V/25)^{1/\beta} = (V/250)^{1/\beta'}. \quad (11)$$

Numerical values of  $\alpha$  and  $\beta$  are calculated, assuming  $V_0$  to be 250 ml, for different values of  $\alpha'$  and  $\beta'$  chosen to correspond to the range of our experimental values. For each of these cases, the calculations are made for three different final volumes, 1.25, 2.50 and 5.00 ml.

The calculations show [5] that our electrolysis with periodic additions gives a tritium recovery which is roughly 15% less than that in an equivalent conventional batch electrolysis. The result to be used together with equations (1) to (3) is

$$\eta = \log \beta / \log \alpha = 1.337 \pm 0.007. \quad (12)$$

#### (b) INFLUENCE OF VAPOUR PRESSURE AND SPRAYING

During electrolysis the gases bubbling through the liquid and escaping from the system carry away both water vapour and spray. The differential quantities in equation (1) are thus each composed of three terms, created by the electrolytical disintegration, by the vapour loss and by the spray loss. We denote the purely electrolytical enrichment factors by  $\alpha_0$  and  $\beta_0$ , the vapour pressure of ordinary water by  $b$  atm, the barometric pressure by  $b$  atm. The relative vapour pressures of HDO and of HTO to that of water at the same temperature are  $f_D$  and  $f_T$ , respectively. Furthermore, we presume  $s$  moles of water being carried away as droplets per mole of electrolytically disintegrated water. After some deductions and approximations [5] equivalent to those incorporated in equation (2), we arrive at

$$\alpha = \frac{1 + 1.5 b' + s}{1/\alpha_0 + 1.5 b' f_D + s}, \quad (13)$$

$$\beta = \frac{1 + 1.5 b' + s}{1/\beta_0 + 1.5 b' f_T + s}, \quad (14)$$

where

$$b' = b/(b - h). \quad (15)$$

We have made some experiments in which the released gases were trapped in a cotton-wool filled cold trap or in a drying agent and have determined the sum of  $(1.5 b' + s)$ . The highest value of  $s$  obtained in our 3 A electrolysis was 0.003, but in most cases we found  $s = 0$  within the limits of error. In the computations below we thus neglect  $s$ .

TABLE II  
CALCULATION OF THE TRUE ELECTROLYTICAL ENRICHMENT FACTORS  
 $\alpha_0$  AND  $\beta_0$

$\alpha$	$\beta$	$\alpha_0$	$\beta_0$	$\log \beta_0 / \log \alpha_0$
4.00	6.383	4.215	6.965	1.349
6.00	10.975	6.564	13.03	1.364
8.00	16.12	9.100	21.21	1.383
10.00	21.73	11.85	32.44	1.407

Table II gives calculated values of the different parameters at 10°C when  $\alpha$  varies within our experimental range and  $\eta = 1.337$ . For the vapour pressure of water,  $b = 0.01252$  atm is used; and  $f_D = 0.920$  and  $f_T = 0.846$ , the relative vapour pressures of HDO and HTO, are taken from KIRSCHENBAUM [6].

It is seen that  $\eta_0$  is very close to 1.40 as predicted by BIGEISEN [4] but that low  $\alpha_0$ -values tend to decrease this value slightly.

## Conclusion

Our electrolytic enrichment procedure with periodic addition of the water gives apparent enrichment factors for deuterium,  $\alpha'$ , and for tritium,  $\beta'$ , which vary in such a way that the following relationship holds true:

$$\eta' = \log \beta' / \log \alpha' = 1.369 \pm 0.006,$$

when used at 10°C if the sample is brought into the reaction vessel in nine portions.

If this result is applied to the conventional batch electrolysis, in which the entire sample takes part in the reaction all the time, the result can be written

$$\eta = \log \beta / \log \alpha = 1.337 \pm 0.007.$$

Of especially great theoretical interest are the purely electrolytical enrichment factors  $\alpha_0$  and  $\beta_0$ , i. e. the factors referring to the mere electrolytical disintegration of the water molecules. If we correct our experimental results for vapour loss we get

$$1.35 < \log \beta_0 / \log \alpha_0 < 1.41$$

when

$$4 < \alpha_0 < 12.$$

This result is in excellent agreement with BIGELEISEN's [4] predictions from theoretical considerations that  $\log \beta_0 / \log \alpha_0 = 1.40 \pm 0.01$ .

## ACKNOWLEDGEMENTS

The experimental work was performed during 1959 and early 1961 at the Radioactive Dating Laboratory in Stockholm and was made possible by grants from Knut and Alice Wallenbergs Stiftelse and from the United States Atomic Energy Commission, through the International Meteorological Institute of the University of Stockholm. The treatment of the data was done at the Marine Laboratory of the University of Miami (Contribution No. 339) on a grant from the United States Navy. Dr. J. Bigeleisen has kindly given us access to his theoretical results before their publication in these proceedings.

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## DISCUSSION VIII

B. Gonsior (Federal Republic of Germany): Did Prof. Östlund run the apparatus at constant current or at constant specific current per cm<sup>2</sup>?

H. G. Östlund (Sweden): For the enrichment of 250 ml down to about 25 ml, the current density is virtually constant at 0.09 amp/cm<sup>2</sup>. In some cases, this depends on the time during which we allow the surface of the liquid to creep down on the electrode, but that should be the order of less than 5% of the total electrolyzing time and should be equivalent to a rise in current density from 0.09 to 0.14 a/cm<sup>2</sup>, or something in that range. Thus, it is virtually constant all the time.

**J. Bigeleisen** (United States of America): I would like to make some remarks on Prof. Östlund's very interesting experiments and they apply equally well to experiments in which the tritium is concentrated to such an extent that the deuterium content is brought up to over 90%. The elementary separation factor is independent of the concentration on an atomic basis, which is true to a very good approximation. In experiments of very high precision, there will be slight deviation because the elementary enrichment factors will depend on the concentration of deuterium and tritium in the system. This will be a small effect, however, but where very careful experiments are concerned one would either have to correct for it or else restrict oneself to weaker enrichment concentrations less, say, than 10—20% deuterium.

# THE RECONCENTRATION OF TRITIUM BY DISTILLATION

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Abstract — Résumé — Аннотация — Resumen

**The reconcentration of tritium by distillation.** A method of tritium reconcentration by the total reflux distillation of water under reduced pressure using random-packed columns was investigated.

For the maximum removal of tritium from a one liter reservoir, operating periods of several weeks were required. For this a fully automatic fractionating system incorporating an apparatus for taking samples automatically under reduced pressure was developed to enable the distillation to proceed with the minimum of manual adjustment. To reduce the possibility of flooding at the base of the column due to gravity settling of the packing over long periods of time, a novel design feature was incorporated at the junction of the column and the reflux meter.

The performance of several commercially available column packings was investigated in an aqueous environment. Details of the packing pre-treatment to inhibit maldistribution in a liquid of high surface tension are given and enrichment factors calculated.

A low H.E.T.P. (height equivalent to a theoretical plate) of about 0.8 in has been achieved with pre-treated phosphor-bronze gauze rings in an aqueous environment. With a reservoir-to-boiler volume ratio of the order of 7 : 1, a maximum of 98% of the tritium in the reservoir was removed in 28 d continuous distillation with a throughput of 100 ml/h. This indicated a tritium reconcentration factor of 6.3. By increasing the throughput to 140 ml/h, 92% of the tritium was extracted in 11 d.

The reproducibility of the reconcentration factor with time was, however, shown to vary, and the reasons for this are discussed in the paper.

**La reconcentration du tritium par distillation.** Les auteurs ont étudié une méthode de reconcentration du tritium par distillation de l'eau sous reflux total et à pression réduite, avec utilisation de colonnes dont le garnissage était disposé au hasard.

Pour extraire un maximum de tritium dans un réservoir d'un litre, il a fallu opérer pendant plusieurs semaines. A cet effet, les auteurs ont mis au point un appareil de fractionnement entièrement automatique muni d'un dispositif automatique de prise d'échantillons à pression réduite, afin que la distillation puisse se poursuivre avec un minimum d'ajustement manuel. Pour réduire la possibilité d'obturation par le liquide à la base de la colonne par suite du tassement naturel du remplissage au cours de périodes prolongées, on a introduit un dispositif de conception nouvelle au point de jonction de la colonne et du compteur à reflux.

Les auteurs ont étudié en milieu aqueux l'efficacité relative dans les colonnes de plusieurs garnissages que l'on trouve sur le marché. Ils donnent des détails du traitement préalable auquel on soumet les garnissages pour empêcher une distribution défavorable dans un liquide de forte tension superficielle, ainsi que les résultats du calcul des facteurs d'enrichissement.

En utilisant en milieu aqueux des anneaux en toile de bronze phosphoreux ayant subi un traitement préalable, ils ont pu obtenir une faible H.E.P.T. (hauteur équivalente à un plateau théorique) d'environ 0,8 pouce. Le rapport entre le volume du réservoir et celui de la chaudière étant de 7 à 1, ils ont extrait un maximum de 98% du tritium du réservoir par distillation continue pendant 28 jours avec un débit de 100 ml/h, ce qui correspond à un facteur de reconcentration du tritium de 6,3. En portant le débit à 140 ml/h, ils ont pu extraire 92% du tritium en 11 jours.

Les auteurs ont cependant constaté qu'en opérant dans les mêmes conditions d'expérimentation il n'est pas toujours possible d'obtenir le même facteur de reconcentration; ils examinent dans le mémoire les causes de ce phénomène.

**Реконцентрация трития дистилляцией.** Был исследован метод реконцентрации трития путем общей орошаемой дистилляции воды под пониженным давлением с применением случайно насадочных колонн.

Для максимального удаления трития из резервуара емкостью в 1 литр был необходим рабочий период в несколько недель. С этой целью была разработана полностью автоматическая фракционная система, включавшая в себя прибор для автоматического взятия образцов под пониженным давлением, с тем чтобы дистилляция проходила при минимуме ручной работы. Для сокращения возможностей захлебывания основы колонны, которое происходит вследствие давления осадка насадки в течение длительного времени в месте соприкосновения колонны и орошающей воды, было сделано еще одно новое приспособление.

Свойства некоторых имеющихся в продаже насадок колонн были исследованы в водных условиях. Даются подробности предварительной обработки насадки для устранения нарушения распределения потока в жидкости с высоким поверхностным натяжением и учитываются факторы обогащения.

При использовании в воде предварительно обработанных металлических колец из фосфора и бронзы низкая высота колонны, эквивалентная одной теоретической тарелке, составила около 0,8 дюйма. При соотношении между резервуаром и бойлером порядка 7:1 максимум 98% трития, находящегося в резервуаре, устраняется посредством непрерывной дистилляции в течение 28 дней при пропускной способности 100 миллилитров в час. Это определяет коэффициент реконцентрации трития, равный 6,3. При увеличении пропускной способности до 140 миллилитров в час было удалено 92% трития в течение 11 дней. Однако указывается, что со временем воспроизводимость коэффициента реконцентрации варьируется, и в докладе обсуждаются причины этого.

**Reconcentración del tritio por destilación.** Los autores estudian un método de reconcentración del tritio por destilación de agua a refujo total y presión reducida, utilizando columnas de relleno no ordenado.

Para extraer la máxima cantidad de tritio de un depósito de un litro, fueron precisas varias semanas de funcionamiento. Para ello se ha ideado un sistema de fraccionamiento totalmente automático, provisto de un dispositivo para tomar muestras a presión reducida, con objeto de poder efectuar la destilación con el mínimo de ajustes manuales. A fin de evitar la posibilidad de obturación por el líquido en la base de la columna, debido al asentamiento del relleno por gravedad cuando éste se utiliza durante mucho tiempo, se ha introducido un dispositivo de nuevo tipo en la unión de la columna y del contador de refujo.

Los autores estudian el rendimiento en medio acuoso de algunos productos de relleno, de venta en el comercio. Asimismo, describen detalladamente el tratamiento previo del relleno para evitar la distribución desfavorable en un líquido de tensión superficial elevada, y calculan los factores de enriquecimiento.

Utilizando en un medio acuoso anillos de malla de bronce fosforado, previamente tratados, se ha logrado reducir la altura equivalente a la de un plato teórico, a unas 0,8 pulgadas. Con una razón del orden de 7:1 entre el volumen del depósito y el volumen de la caldera se ha extraído, como máximo, un 98 por ciento del tritio contenido en el depósito, en 28 días de destilación continua, trabajando con un caudal de 100 ml/h. Es decir, el factor de reconcentración del tritio es de 6,3. Aumentando el caudal a 140 ml/h, se ha extraído el 92 por ciento del tritio en 11 días.

Se ha comprobado que aun cuando las condiciones experimentales permanecen iguales, no siempre es posible obtener el mismo factor de reconcentración. En la memoria se examinan las causas de esta variación.

## Introduction

The tritium concentration in surface water is of the order of one tritium atom in  $10^{18}$  protium atoms (known as one Tritium Unit, 1 T.U.) which gives rise to



7 disintegrations/min per l of water. For "age" determinations of water reservoirs cut off from surface replenishment, the measurement of even lower specific activities is required. It is not possible to measure such low activity directly so reconcentration of the tritium is necessary.

Of the four main methods of reconcentration, electrolysis, distillation, thermal diffusion and gas chromatography, only the first two are considered here. Although tritium is normally reconcentrated by electrolysis, a few quantitative investigations of the value of the distillation method have been made [1, 2, 3], but published information on the techniques of distillation of aqueous systems on a laboratory scale is somewhat limited.

The most important characteristic of a tritium reconcentration technique to be used in the determination of the age of water is that of reproducibility. This is limited in electrolysis by the reproducibility of electrode surfaces and their changes during operation. In an investigation of the parameters of reproducibility and tritium loss for the distillation technique a completely self-contained, fully automatic distillation process for operation at reduced pressures was developed. The apparatus was developed with the intention of extracting the tritium from water samples of up to 10 l into a volume of about 100 ml. Further reduction into a volume of about 1 ml, suitable for gas or scintillation counting, could be undertaken by small scale distillation or electrolysis.

### Theoretical considerations

If a mixture of ordinary water ( $H_2O$ ) and tritiated water (HTO) is boiled, the ordinary water will vaporize preferentially because of its higher vapour pressure. Isotopic separation is then possible by distillation through a fractionating column, which combines the repeated processes of simple distillation in a single unit.

The column was filled with a packing to promote intimate vapour-liquid contact. The vapour was condensed after being passed up the column, and the condensate was allowed to displace its own volume of water from a reservoir. This displaced water was returned to the column head and flowed down the column to provide reflux for the ascending vapour. Efficient molecular and heat transfer can occur between the liquid and vapour phases on the large surface area provided by the packing in the column. As a result, the vapour became enriched with the more volatile component from the down-flowing liquid, and the less volatile component (in this case, the tritiated water) was concentrated towards the base of the column. When the distillation had been taken to equilibrium, the water in the boiler was enriched in tritium and the tritium-depleted water was in the reservoir.

To express column performance the term "theoretical plate" is used. This can be defined by consideration of the vapour above a boiling liquid which consists of two components of different vapour pressure. The enrichment of the more volatile component in liquid formed by condensation of the vapour is equivalent to the enrichment obtained by distillation through a column of one theoretical plate. In a random packed distillation column the length equivalent in fractionating effect to a theoretical plate is termed the height equivalent of a theoretical plate (H.E.T.P.) and is found by division of the height of the column by the number of theoretical plates.

For practical determination of the number of theoretical plates the enrichment factor for a packing was first determined with tritium samples which could be counted directly by a coincidence liquid scintillation technique (CAMERON [4]). The enrichment factor is defined as the ratio of the concentrations of the com-

ponents at the column base divided by their ratio at its head when equilibrium has been reached. For an ideal mixture under total reflux the following equation may be applied at equilibrium:

$$\alpha^{n+1} = \frac{\frac{\text{HTO}}{\text{H}_2\text{O}} \text{ column base}}{\frac{\text{HTO}}{\text{H}_2\text{O}} \text{ column head}}$$

where  $\alpha$  is the ratio of the vapour pressures of the two components (the relative volatility) and  $n$  is the number of theoretical plates. The relative volatility increases as the temperature decreases, and the ease with which the two components can be separated increases at reduced temperature (and pressure). Values of the relative volatility measured by SEPALL and MASON [5] (1.08 at 33 °C) were used in the calculation of the H.E.T.P. for the different packings investigated.

### Experimental investigation

The investigation fell broadly into two parts: the development of an automatic technique for extended operation at reduced pressures and the treatment of commercially available packings for use in an aqueous environment.

### The apparatus

The apparatus consisted of five sections: the boiler, the column, the condenser, the reservoir and the associated automatic pressure control and sampling systems.

#### THE BOILER

The boiler comprised a three-necked round-bottom 250 ml heat-resisting glass flask, into the bottom of which was sealed a glass capillary tube of 1-mm bore for sampling purposes. The boiler was lagged with glass wool to reduce heat losses so that a constant boil-up rate could be maintained. A 200 W-lagged heating mantle provided the principal heat supply to the flask. To inhibit superheating and consequent irregular boiling at reduced pressures, a local hot spot in the form of a platinum heating coil was used. The heat-input from this was controlled by a variable transformer and for smooth ebullition was generally maintained at about 100 W. A further aid to controlled boiling at reduced pressures was obtained by the use of a small piece of polytetrafluorethylene ("Teflon") in the boiler [6].

The boil-up rate was measured by a lagged reflux meter between the boiler and the base of the column. The design of this meter is shown in Fig. 1. By magnetic location of a stainless steel ball in the ground glass seating, the water-flow to the boiler was temporarily restricted and the volume of water appearing in the calibrated chamber was measured. As the system was at total reflux, this is the boil-up rate. The glass septum was incorporated in the meter to stop jets of liquid being ejected into the base of the column in case sporadic superheating should occur during extended operation. A mercury filled thermometer-pocket containing a thermometer calibrated to 0.1 °C was used to measure the vapour temperature in the boiler.

An independent rough check on the boil-up rate was obtained from the heat balance for the cooling water in the condenser, it being assumed that at equilibrium the condensation rate in the condenser was equal to the evaporation rate in the boiler. Agreement with the reflux meter was within 10%. Errors introduced by

heat input to the column jacket and the vapour heater above the column were estimated to be about 2%.

Other apparatus for producing stable ebullition at reduced pressures was of the flash boiler type. One consisted of a platinum heating coil in a porous tube closed at one end and fitted inside the boiler to restrict the volume of water available for

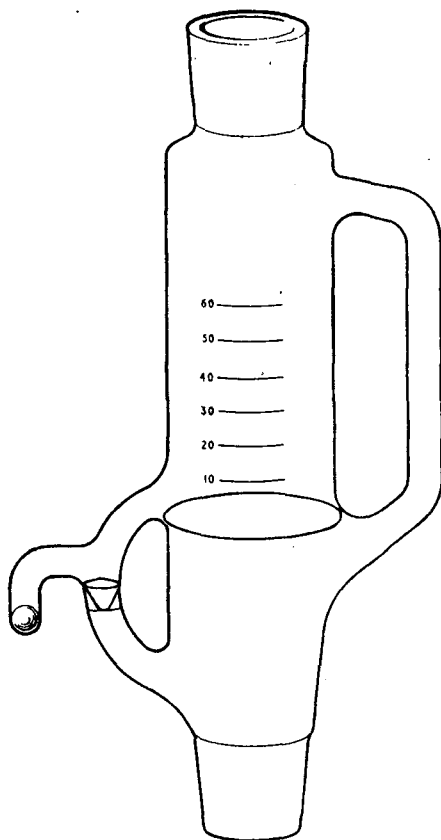


Fig. 1  
Reflux meter.

vaporization at any time by the diffusion of water through the walls of the porous tube. Immediate vaporization of the liquid occurred when it came into contact with the hot coil. A further development which gave stable ebullition at reduced pressure incorporated a side loop between the bottom and the top of the boiler. The vertical section of the loop comprised a 1-cm bore silica tube overwound by an electrically heated Nichrome coil which acted as a flash boiler (Fig. 2). The vapour from the side loop was passed into the liquid in the heated boiler, producing efficient agitation and steady ebullition. This method was used successfully for two distillations but was temporarily discontinued so that a more suitable mechanical construction could be made. It is intended that this technique be incorporated in a larger distillation unit at present under construction.

## THE COLUMN

The column, which is shown diagrammatically in Fig. 3, comprised 5 ft of 1-in bore heat-resisting glass tubing. The base of the column was designed to inhibit flooding, which may occur at high through-put rates or when the packing compacts during extended operation. The lower end of the column was sealed into a 1.5-in

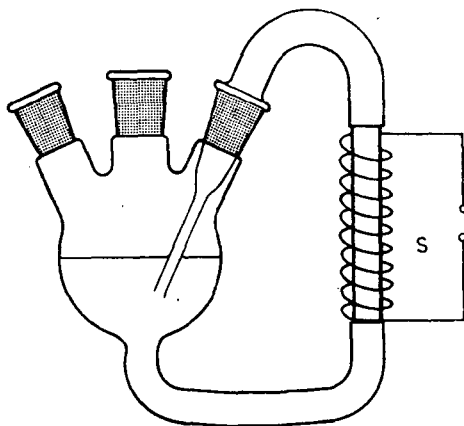


Fig. 2

Boiler for operation at reduced pressures.  
S - Silica tube overwound with a Nichrome heating coil.

diameter glass tube 3.5-in in length. The part of the column projecting into the larger tube had 12 1/16-in diameter holes equispaced around the circumference to act as inlets for the ascending vapour phase (Fig. 3A). The descending liquid flowed past these holes and emerged from the packing past the glass spiral which supported it. The column was packed to a length of 5 ft with the different packings to be tested. At the top of the column a Nichrome spiral spring was used to inhibit movement of the packing at high vapour loading.

The column was enclosed in a glass jacket surrounded by an electrically-conducting, heat-resisting glass tube, which served as a heating jacket. The heat input to the tube was controlled by a variable transformer and adjusted to balance heat losses from the column. To complete the insulation a resinated fibre glass jacket surrounded the outer column jacket. The temperature in the annulus between the column and the inner jacket was constant to within  $\pm 0.9^{\circ}\text{C}$  during extended running, and the heat-resisting glass tube heater was adjusted to maintain this annulus at  $1^{\circ}\text{C}$  above distillation temperature. The vapour temperature at the head of the column was measured by a thermometer calibrated to  $0.1^{\circ}\text{C}$  in a lagged mercury-filled thermometer pocket.

The pressure drop between the base and head of the column was measured by a mercury-filled U-tube manometer (Fig. 3).

## THE CONDENSER

An efficient 30 cm water-cooled condenser was used and was lagged with asbestos so that a heat balance could be made on the cooling water. The tube connecting the column head to the condenser was heated by an electrical heating tape so that condensation of the vapour before it entered the condenser was inhibited. Thermometers

calibrated to within  $0.1^{\circ}\text{C}$  were used to measure the temperature of the water entering and leaving the condenser.

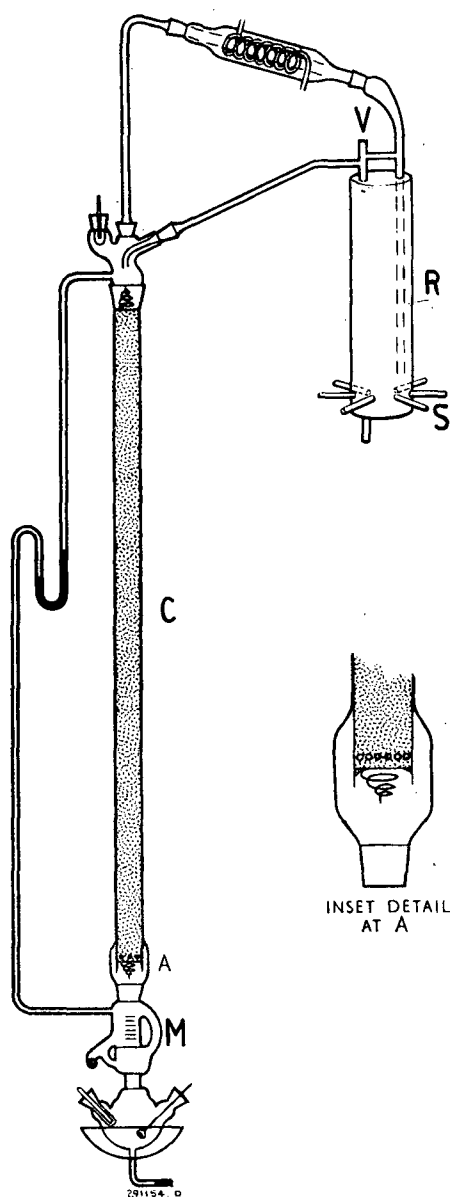


Fig. 3

Diagram of apparatus.

C, Packed Column. R, Reservoir. S, Sampling Ampoules. M, Reflux Meter.

## THE RESERVOIR

The reservoir was a copper cylinder of 2-in diameter and 1.2-l capacity. The output of the condenser flowed into an inlet tube at the top of the cylinder, which was extended inside the cylinder so as to discharge the condensate near the base. The incoming liquid displaced water from the top of the reservoir over a weir to the head of the column. The pressures between the inlet and outlet tubes of the reservoir were equalized to inhibit siphoning and to produce a steady return flow of water to the column.

Two inches from the base of the reservoir six copper capillary tubes of 1-mm bore measuring 0.25 cm in length and diameter were sealed into the reservoir, equispaced around its circumference. These were the sampling points for the automatic sampling system.

A tube at the base of the reservoir allowed it to be filled with the water sample at the start of an experiment. It also acted as a drain on completion of a period of distillation.

## THE AUTOMATIC PRESSURE CONTROL AND SAMPLING SYSTEM

The pressure in the apparatus was controlled automatically by a mercury-filled U-tube twin-contact manostat operating an electro-magnetic valve via a relay. One of the manostat contacts was an adjustable tungsten wire so that the pressure could be set to a pre-determined value. So that distillation could proceed with the minimum manual attention, a 10-l brass vacuum reservoir was evacuated automatically at pre-set intervals. Any rise in pressure in the apparatus caused the electromagnetic valve to function, momentarily connecting the apparatus to the evacuated reservoir via a 0.5-l flask. This flask was used to reduce the rate at which the pressure was returned to its pre-set value, as sudden pressure changes adversely affect the operation of the column at reduced pressures.

Samples were extracted from the apparatus by the following technique suggested by EVELEIGH [7]: six glass ampoules containing wax seals were attached by short lengths of pressure rubber tubing to copper sampling points to form close butt-joints. Samples were taken by melting of the wax seal with a small Nichrome heating coil actuated automatically at a pre-determined time by the circuit shown in Fig. 4. The ampoules were constructed by sealing a 1-mm bore glass capillary tube 2 cm in length onto an open-ended 0.5-cm internal diameter glass tube 9.5 cm in length (Fig. 5). A small pellet of Edwards W wax (melting point 80 °C) was placed in the composite tube and shaken so as to lie at the junction of the capillary and glass tubes. The open end of the 0.5-cm tube was then sealed off. The sealed ampoule was evacuated to a pressure of about 50  $\mu$  and the wax pellet melted *in situ* at the neck of the ampoule by an external heating coil. On cooling, the wax made a vacuum-tight seal at the neck of the ampoule (Fig. 5). After sampling had taken place by automatic operation of heating coils around the necks of the ampoules, the wax was cooled by the water on both sides and formed a seal between the sample and the reservoir. This precluded any mutual diffusion between the sample and the reservoir. The ampoules were removed from the rubber tubes by tightening a spring clip in place at the junction of the glass and copper capillary tubing. The ampoule was removed and replaced by a new one, the clip released and the ampoule pushed up to make a butt-joint with the copper capillary tube. The entire operation was performed without the ingress of air to the reservoir.

All joints in the apparatus were made vacuum-tight with Edwards W wax or

with standard vacuum couplings. The use of grease or low melting point waxes is precluded by the risk of contamination of the packing and internal glass surfaces.

With these techniques it is possible to perform continuous distillation at reduced pressures for periods of up to 50 d.

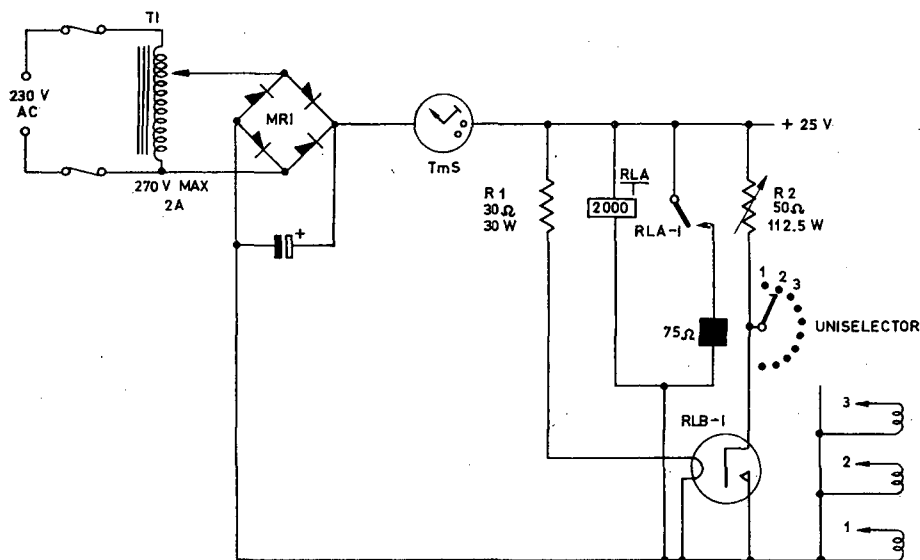


Fig. 4

Circuit for the automatic sampling apparatus.

### Packings and results

Three random packings were investigated: Fenske helices and Borad and Dixon rings.

#### THE FENSKE PACKING

The Fenske helices used consisted of 0.018-in diameter glass rod in the form of single coils 5/32-in in diameter. Before insertion into the column they were



Fig. 5

Sampling Ampoule.

W, Wax Seal. G, Ground Glass Taper.

cleaned by refluxing in 4N nitric acid for several hours and then washed in distilled water. After the column was loaded, the packing was refluxed *in situ* with acetone and diethyl ether to remove any organic contamination and finally was air dried.

The packing flooded during operation at boil-up rates of 50 to 80 ml/h, and maldistribution of the liquid phase was very marked during distillation with water. For improvement of the wetting characteristics of the helices they were refluxed in

a mixture consisting of 5% of hydrofluoric acid and 60% nitric acid and water to etch the surfaces of the glass helices.

The efficiency of this packing was investigated with the apparatus operating at a boil-up rate of 60 ml/h and a distillation pressure of 15 cm Hg. The volume of the reservoir was 800 ml and that of the boiler 250 ml. The packed column contained about 40 ml of static hold-up.

At this time the reservoir was a round-bottom flask which allowed some condensate to flow back to the column head without displacement of the water from the reservoir and hence was inefficient in operation. Manual sampling of the reservoir and boiler liquids involved bringing the apparatus to atmospheric pressure, thereby upsetting the condition of distillation.

Equilibrium was reached in 10 d and conditions remained constant for a further 22 d. An enrichment factor of two was obtained in the boiler, and about 20% of the tritium was removed from the reservoir. The column was operating with 12.7 theoretical plates and had an H.E.T.P. of 4.4 in.

#### THE BORAD RING PACKING

The Borad rings investigated comprise a double-wall cylinder of phosphor-bronze square-wave gauze with a  $\Theta$  cross-section. The rings had a diameter and length of 1/8 in and were fabricated from 0.006 in-diameter wire woven at 50 strands to the inch; they operated by retaining a liquid film in the mesh by surface tension so that their performance was dependent on their wettability and cleanliness.

Organic contamination was removed by refluxing with acetone and diethyl ether, followed by air drying. The technique of pre-flooding the packings at the start of a distillation to ensure thorough wetting of the packing and high efficiency was attempted on several occasions. The procedure proved difficult to control over a period of time sufficient to attain adequate wetting of the packing and was discontinued in favour of allowing the packing to "wet-up" during the course of distillation.

With this system of water distilling, channelling and maldistribution of the liquid phase was evident, but an improvement occurred after the surfaces of the rings had been oxidized. Initially atmospheric oxidation at 150°C was tried but was later superseded by a chemical method which gave better control. The rings were immersed in a 10% solution of potassium persulphate to which a few drops of silver nitrate had been added to catalyze the oxidation. When the packing had been boiled in this solution for 2 h, a matt grey-black oxide film developed on the surface. The packing was then washed with distilled water to remove any excess oxide particles from the mesh. After air drying, the column was packed with the treated rings by vibration during loading. A 10% improvement in compaction resulted. For completion of the pre-treatment of the rings, they were refluxed *in situ* with ethylene glycol monoethyl ether, which was then removed by refluxing with water. A final air drying of the packing completed the process.

The results of two distillations are shown in Table I. Run 1 was carried out to equilibrium (Fig. 6), which was reached after about 40 d. A large reservoir-to-boiler volume ratio was used and an enrichment factor of 15 was obtained. After equilibrium had been reached on the 47th day, 30 ml of water was extracted over a period of 2 h from the reservoir whilst the distillation was in progress, thereby reducing the boiler volume from 90 ml. After 3 d the enrichment factor in the boiler was 19. Run 2 was operated with a smaller reservoir and a higher through-put and



TABLE I  
BORAD PACKING RESULTS

Run No.	Distillation Period (d)	Through-put (mean) (ml/h)	Column head pressure (cm)	Reservoir volume (ml)	Boiler volume (ml)	Final enrichment in boiler	Tritium extraction from reservoir %	Column hold-up (ml)	H.E.T.P. (5 ft column) (inches)	Remarks
1	50	65	6.5	2550	90	15	87	57	1.54	Equilibrium
2	5	130	4.5	1200	42	8.3	56	67	—	Not equilibrium

TABLE II  
DIXON PACKING RESULTS

Run No.	Distillation Period (d)	Through-put (mean) (ml/h)	Column head pressure (cm)	Reservoir volume (ml)	Boiler volume (ml)	Final enrichment in boiler	Tritium extraction from reservoir (%)	Column hold-up (ml)	H.E.T.P. (5 ft column) (inches)	Remarks
1	6	125	6.5	—	—	3.7	86	—	—	Not equilibrium
2	28	100	4.0	1200	150	6.3	97.5	255	0.75	Equilibrium
3	11	140	4.0	1200	150	4.4	92.5	180	1.04	Near equilibrium

showed rapid enrichment, but equilibrium was not reached because of mechanical failure.

Packing of smaller size was expected to be more efficient than the  $1/8$ -in Borad rings. Further work was carried out on the  $1/16$ -in Dixon rings to test this expectation.

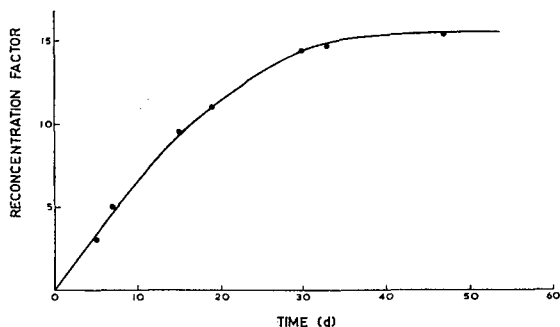


Fig. 6

Graph of the variation of reconcentration factor with time for Run 1.

#### THE DIXON RING PACKING

The Dixon rings consisted of single-wall cylinders of phosphor-bronze square-weave gauze with a  $\Theta$  cross-section. The rings had a diameter and length of  $1/16$ -in and were fabricated from 0.004 in-diameter wire woven at 100 strands to the inch. Like the Borad rings, they operated by retaining a liquid film in their interstices under surface tension. The smaller rings packed more compactly than did the larger Borad rings and resulted in less channelling and reduced maldistribution of the liquid phase down the column wall [8]. The finer mesh and smaller wire diameter also assist the retention of a liquid film in the interstices of the packing at low vapour velocities. The rings were used in the oxidized condition and were packed into the column by a vibration technique, as before.

The results of three distillations are shown in Table II. The percentage removal of tritium from the reservoir was generally greater than that attained with Borad packing. The enrichment in the boiler was smaller, partly because of the larger volume of liquid in the boiler and partly because of the increased hold-up of the finer mesh of the packing.

One run was operated to equilibrium. Automatic sampling ensured the minimum of disturbance to the column operation at reduced pressure. In a run of 28 d, 97.5% of the tritium was extracted from the reservoir. A second distillation with a higher through-put rate was run almost to equilibrium and in 11 d removed 92.5% of the tritium from the reservoir. A comparison of data obtained in these two runs and correction for the different rates of through-put showed the second run to have a slightly higher extraction rate of tritium per unit through-put. If the distillation had been taken to equilibrium, an extraction of more than 97.5% of the tritium from the reservoir would have resulted.

#### Discussion

In an idealized distillation of tritiated water in a column of zero liquid hold-up, the specific activity of the liquid in the reservoir decreases as that in the boiler

increases at a rate determined by the ratio of the volumes of liquid in the reservoir and boiler. Although the total volume in the boiler and column is constant, the ratio of the volumes is not necessarily constant during operation. In practice, therefore, allowance must be made for the unknown specific activity of the water held up in the packing. It follows that the specific activity of the liquid in the boiler is not an accurate representation of the performance of the column. In order that virtually all the tritium in the sample be reconcentrated into the final reduced volume, the liquid draining from the column must be included with that in the boiler.

The most important parameter which must be reproducible is the ultimate percentage of tritium which can be extracted from the reservoir into the column and boiler.

Future improvements in the distillation technique for extraction of tritium from water are aimed at extraction of at least 97.5% of the tritium from the reservoir and establishment of reproducibility.

Better extraction at equilibrium might be obtained by an increase in the number of theoretical plates in the column, but the increased height of the column would increase the liquid hold-up, which might offset this advantage. Slightly improved performance might result from the use of liquid redistribution sections placed at intervals in the column. Thus, short sections of Multifil might be useful in correction of the tendency of Dixon rings to distribute the liquid phase towards the walls of the column, as this packing tends to have the reverse effect.

Higher extraction can be obtained by performance of the distillation at lower temperatures, thereby increasing the relative volatility of the system. As the distillation pressure is lowered to obtain the lower boiling point, irregular ebullition occurs and the velocity of the vapour phase in the column is increased. Because of this, the processes of mass and heat transfer in the column are impaired and the H.E.T.P. is increased once a critical vapour velocity is exceeded. There is consequently a limit to which the pressure can be lowered if effective distillation is to take place.

The time taken to attain equilibrium can be reduced by increase of the boil-up provided that the critical vapour velocity of the vapour is not exceeded. It is probable that a considerable reduction in the equilibrium time can be made by this means in the present apparatus.

Further reconcentration and volume reduction will be required for counting of the tritium sample. This may be carried out with electrolysis, which is more suitable for small samples. When operating with a sample volume of about 100 ml, the electrolysis cell can be run at a low rating, and the process can be made more reproducible. This reproducibility will determine the extent to which the fractionation technique will need to be developed so that it produces less error than the reconcentration by electrolysis.

This is a preliminary paper outlining the techniques used in the fractional distillation of water and summarizing the results so far obtained. Should it prove difficult to obtain effective reproducibility, then bubble-cap or sieve-plate columns suitably modified for the distillation of aqueous components may be more suitable.

## Conclusions

With the fractional distillation apparatus developed during the investigation, 1/16-in oxidized Dixon rings proved the most satisfactory of the three random packings investigated for the extraction of tritium from water. With a one-inch bore column 5 ft in length, up to 97.5% of the tritium content of the distillation reservoir was extracted during a distillation to equilibrium. Preliminary results

indicate that this extraction may be reproducible, but further investigation is necessary to assess the limits of reproducibility.

With a distillation apparatus capable of reproducibly extracting almost all the tritium from the reservoir, unknown samples of tritiated water can be enriched. The enriched samples would consist of all the water in the boiler and the water held up in the column. Since all this volume can be measured and the volume of the reservoir is known, the enrichment factor for the sample can be calculated. For extraction of 97.5% of the tritium from the reservoir, the enrichment factor E.F.' for the enriched liquid would then be redefined as

$$E.F.' = \frac{0.975 (\text{Reservoir volume}) + (\text{Boiler volume} + \text{column hold-up volume})}{\text{Boiler volume} + \text{column hold-up volume}}$$

If the extraction was such that 5% of the tritium remained in the reservoir instead of 2.5% as in the above example (i. e. a factor of two), then the final error in E.F.' would only be 2.5%.

### ACKNOWLEDGEMENTS

We are grateful to Professor E. D. Hughes and Dr. C. A. Bunton of University College, London, Professor S. R. M. Ellis and Mr. K. Porter of Birmingham University and Dr. B. Giletti of Oxford University for helpful discussions.

We also wish to thank Dr. P. T. Walker, Mr. J. W. Eveleigh and Mr. H. E. Dobbs of the UKAEA for their useful advice.

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### DISCUSSION IX

**J. Varshavsky** (Union of Soviet Socialist Republics): It is well known that the separation factor is not dependent on vapour pressure alone. I should therefore like to ask Mr. Rawson if he is certain that the separation factor ratio for H<sub>2</sub>O, HDO and HTO really remains strictly constant during the process. What could exert a disruptive effect on the relationship between these factors?

**D. Rawson** (United Kingdom): I think that a satisfactory answer to this question can be obtained by reference to Mr. Bigeleisen's paper on page 161 in which the variation of the

$$\frac{\ln P_{H_2O}/P_{HTO}}{\ln P_{H_2O}/P_{HDO}}$$

is given with temperature.

**J. Bigeleisen** (United States of America): I would like to ask Mr. Rawson

whether, in his experiment, he monitored the deuterium concentration during distillation.

**D. Rawson:** We have not measured any deuterium concentrations during distillation, although I agree that this would be a very valuable additional calibration. I should explain that the column was spiked, i. e. we started off with a known specific activity in both the reservoir and the boiler, and this activity was such that we were able to monitor the change in concentration directly as the distillation proceeded by means of liquid scintillation counting. However, deuterium calibration is a step that should be added in the future.

**J. Bigeleisen:** There are two reasons for monitoring deuterium. For one thing, there is a relation between the elementary separation factor for the tritium and for the deuterium and there are some experiments along this line in the work of Avinur and Nir. Secondly, the theory of a column operating at total reflux has been studied in great detail by Cohen and if the column is so operated, with a substance having a small separation factor, it can be shown on the basis of Cohen's theory that the logarithm of the separation of one component to the separation of another component is independent of many kinds of perturbations in the operation of the column, thanks to which one isotope becomes a very good monitor for the other. In fact, a theoretical description of the relative separation is described in a paper by Dr. Ribnikar and myself, which will appear shortly in the *Journal of Chemical Physics*.

**W. R. Biles** (United States of America): I wonder whether Mr. Rawson knows that the Chemical Engineering Department of Pennsylvania State University has, for some twenty years, been studying the distillation of organic (hydrocarbon) systems in packed columns and that they have a considerable amount of data on packing performance. As I remember they were never successful in getting the packings to work efficiently on aqueous systems. Mr. Rawson's success in getting water to wet Dixon rings, and the similarity of his results with their data, might mean that many of their techniques would be useful in his work. In view of the very long time it took for his columns to reach a steady state and the importance, as shown by their work on the equilibration time, of the ratio of through-put to hold-up (not only in the column but above the column) I would suggest that he might achieve the same separation much more quickly by conventional batch distillation, starting up a total reflux and drawing off the material at a high reflux ratio.

One thing I fail to understand is why we speak of enrichment factors. If we know the relative volatility and the characteristics of the packing, we can calculate the separation, either by the Fenske equation or by some more complex equation when the operation is not at steady state. It is easier to remember just one number than a dozen. We should therefore refer only to the relative volatility of these systems.

**D. Rawson:** By running the column as Mr. Biles suggests, equilibrium for total reflux will be established quickly and, providing that the extraction of a small percentage of the reflux does not reduce the number of theoretical plates in the column too seriously, batch operations might well result in more rapid extraction of the tritium from a given volume.

**E. Roth** (France): I would like to ask Mr. Rawson whether he has any fear of sample contamination in the columns at the low level of tritium activity after using a spike. Also, whether he has considered the preparation — by means of distillation — of tritium-free water to serve as a zero standard.

**D. Rawson:** In reply to the first question, cross-contamination could be a factor in the distillation of samples of widely differing tritium content. In practice, decontamination would be carried out by repeated distillation of several samples of the low-tritium-content water to be determined.

As regards the second question, with further development of the distillation technique it might be possible to prepare water of very low tritium content, but there appear to be more readily available natural sources.

# THE SEPARATION OF HYDROGEN TRITIUM AND TRITIUM HYDRIDE BY GAS CHROMATOGRAPHY

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UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

**The separation of hydrogen, tritium and tritium hydride by gas chromatography.** Now that successful separation of hydrogen, deuterium and hydrogen deuteride has been achieved by gas chromatography, similar studies are being made dealing with mixtures of hydrogen, tritium and tritium hydride. Since tritium is used in tracer quantities the usual katharometer cannot be employed for its detection. This difficulty has been overcome by providing immediately following the katharometer a vibrating reed electrometer equipped with a high resistance leak which allows continuous monitoring of the activity of any tritium or tritium hydride emerging from the column by means of synchronized recorders.

Separation of such mixtures has been tested with columns packed with palladium on silica, silica, alumina, and alumina coated with chromium oxide or ferric oxide. No effective separation was obtained with the palladium on silica column. Good separation was achieved with the plain silica column where hydrogen was employed as the carrier gas, but helium failed to elute the isotopes. Satisfactory results were obtained with the coated, partially deactivated alumina packing when helium or neon was the carrier gas, but the best separation was found with a column packing of uncoated activated alumina.

Calibration with helium-tritium mixtures of known activity plus equilibrated hydrogen-tritium mixtures also of known activity allows quantitative estimation of tritium and tritium hydride.

**Séparation de l'hydrogène, du tritium et de l'hydrure de tritium par chromatographie en phase gazeuse.** La séparation de l'hydrogène, du deutérium et du deutériure d'hydrogène par chromatographie en phase gazeuse ayant été réalisée, on procède maintenant à des études semblables sur des mélanges d'hydrogène de tritium et d'hydrure de tritium. Comme le tritium n'est présent qu'en quantités infimes, on ne peut utiliser le catharomètre ordinaire pour le détecter. On a surmonté cette difficulté en faisant suivre le catharomètre d'un électromètre à lame vibrante, muni d'une fuite haute résistance, qui permet de mesurer, à l'aide d'enregistreurs synchronisés, l'activité de toute quantité de tritium ou d'hydrure de tritium sortant de la colonne.

On a essayé de séparer ces mélanges avec des colonnes garnies de palladium sur silice, de silice, d'alumine et d'alumine recouverte d'oxyde de chrome ou d'oxyde ferrique. Aucune séparation effective n'a été réalisée à l'aide de la colonne de palladium sur silice. On a obtenu une bonne séparation avec la colonne de silice, où l'hydrogène servait d'entraîneur; mais l'hélium s'est révélé inefficace pour l'élution des isotopes. L'alumine partiellement désactivée et gainée a donné des résultats satisfaisants lorsque l'entraîneur était de l'hélium ou du néon; mais la meilleure séparation était assurée par une colonne d'alumine activée et non gainée.

L'étalonnage à l'aide de mélanges hélium-tritium d'activité connue, additionnés de mélanges équilibrés hydrogène-tritium d'activité également connue, permet une évaluation quantitative du tritium et de l'hydrure de tritium.

**Разделение водорода, трития и гидрида трития посредством газовой хроматографии.** В настоящее время, когда уже достигнуты значительные успехи в разделении водорода, дейтерия и водородного дейтерида при помощи газовой хроматографии, проводится аналогичное изучение смеси водорода, трития и гидрида трития. Поскольку тритий применяется в качестве индикатора в ничтожно малых количествах, использование обычного кататермометра для его обнаружения не

представляется возможным. Выход из этого затруднения был найден при помощи того, что непосредственно за кататермометром устанавливается вибрационный электрометр, снабженный отводом утечки высокого сопротивления, что позволяет непрерывно следить при помощи синхронизованных записывающих механизмов за активностью трития и гидрида трития при выходе их из колонны.

Разделение таких смесей проверялось на колоннах, заполненных палладием на кремнеземе, кремнеземом, глиноземом и глиноземом, покрытым окисью хрома или окисью железа. На колонне, заполненной палладием на кремнеземе, не было достигнуто эффективного разделения. Хорошее разделение было достигнуто на простой кремнеземной колонне, когда водород использовался в качестве газа-носителя, но гелий не смог элюировать изотопы. Удовлетворительные результаты были получены на колонне, заполненной покрытием и частично дезактивированным глиноземом, когда гелий или неон являлись газом-носителем, но самое лучшее разделение было достигнуто на колонне, заполненной непокрытым активированным глиноземом.

Калибровка со смесью гелия и трития известной активности плюс с уравновешенными смесями водорода и трития также известной активности позволяет проводить количественный анализ трития и гидрида трития.

**Separación del hidrógeno, tritio e hidruro de tritio por cromatografía de gases.** Ahora que, gracias a la cromatografía en fase gaseosa, se ha logrado separar el hidrógeno, el deuterio y el deuterio de hidrógeno, se están realizando estudios análogos con mezclas de hidrógeno, tritio e hidruro de tritio. Puesto que se utiliza el tritio en cantidades apropiadas para la marcación, no es posible emplear el catárametro usual para su detección. Los autores han salvado esta dificultad colocando, inmediatamente después del catárametro, un electrómetro de lengüeta vibratoria, provisto de un escape de alta resistencia que permite medir continuamente por medio de registradores sincronizados la actividad del tritio y del hidruro de tritio que puedan salir de la columna.

Los autores han ensayado la separación de estas mezclas mediante columnas rellenas con paladio precipitado sobre sílice, con sílice, con óxido de aluminio y con óxido de aluminio recubierto de óxido de cromo o de óxido férrico. Con el relleno de paladio precipitado sobre sílice no se logró obtener separación neta. Al emplear hidrógeno como gas portador, la columna de sílice permitió obtener una separación satisfactoria, pero no fue posible eluir los isótopos con ayuda de helio. Las columnas de óxido de aluminio recubierto de óxido de cromo o de óxido férrico, parcialmente desactivado, dieron buenos resultados cuando se empleó helio o neón como gas portador, pero la mejor separación se obtuvo mediante alúmina activada sin recubrimiento.

Para determinar cuantitativamente el tritio y el hidruro de tritio, es preciso calibrar el dispositivo con mezclas de helio y tritio de actividad conocida y, además, con mezclas de hidrógeno y tritio en equilibrio, de actividad también conocida.

## Introduction

In recent months work dealing with the separation of hydrogen isotopes and nuclear spin isomers by gas chromatography has been pursued in several laboratories. A number of articles describing various degrees of separation have appeared [1—5]. The first complete separation of hydrogen ( $H_2^1$ ), deuterium ( $H_2^2$ ) and hydrogen deuteride ( $H^1 H^2$ ) by gas chromatography was accomplished by SMITH and HUNT [6, 7] and by MOORE and WARD [8]. FURUYAMA and KWAN [9] have now reported further separation of the hydrogen ( $H_2^1$ ) into *ortho* and *para* forms simultaneously with the separation of the hydrogen deuteride and deuterium.

A method for the separation of tritium ( $H_2^3$ ) and hydrogen by displacement chromatography from palladium has been described by CHADWICK [10]; in addition, a patent has been granted for the separation of hydrogen from tritium by contact



of a gaseous mixture with finely divided palladium and collection of the evolved fraction when the palladium is gradually heated [11]. GANT and YANG [12] employed gas chromatography with a molecular sieve column and helium as a carrier gas to separate hydrogen, tritium hydride ( $\text{H}^1\text{H}^3$ ) and tritium from mixtures of these gases. The column was maintained at  $-160^\circ\text{C}$  and the eluant gas oxidized over copper oxide at  $600^\circ\text{C}$  before detection in a katharometer in series with an ionization chamber. The mixtures contained about one atom % of the  $\text{H}^3$  isotope.

The present research involves the application to the study of hydrogen-tritium mixtures of those chromatographic methods which have proved efficient for separation and analysis of hydrogen-deuterium mixtures. However, the mixtures were to contain tritium in the low concentrations applicable to tracer work.

## Experimental

The essential features of the chromatographic and detector systems employed in this research were as follows: the carrier gas from a tank was passed through a sampling system, thence through the chromatographic column followed immediately by a katharometer [13] and a 50-ml Borkowski ionization chamber attached to a Cary Model 31 vibrating reed electrometer, thence through a flowmeter followed by an oxidizing unit to convert any hydrogen into water and finally through a trap containing size 5 A Linde molecular sieves. The katharometer and electrometer were connected to synchronized Brown recording potentiometers. A resistor of  $10^{10}\ \Omega$  was installed in the electrometer between the input terminal and the feedback line, thus making possible the use of a flow system through the chamber. Five different columns were employed in this research. They were packed with (a) 43 ft of palladium on quartz [2]; (b) 25 ft of silica gel; (c) 8 ft of alumina coated with chromia [7]; (d) 8 ft of alumina coated with ferric oxide [8]; and (e) 8 ft of uncoated alumina. Each packing was contained in copper tubing of either 1/4 or 5/16-in outside diameter, and the tubing was coiled in such a manner that it could be immersed in a Dewar flask containing liquid nitrogen or in a constant temperature furnace. Carrier gases employed were hydrogen, helium, neon and argon.

Twenty-five curies of tritium gas (10.7 standard  $\text{cm}^3$ ) of 99 + % purity was obtained in a small metal tank from the Oak Ridge National Laboratory. This was repackaged in 25 7.1 cm long ampoules of 6 mm heat resisting glass tubing, each of which contained 0.89  $\text{cm}^3$  of tritium at 0.5 atm pressure.

For use in the chromatographic experiments a 1-c ampoule of tritium was added to 4000 standard  $\text{cm}^3$  of hydrogen and the mixture stored in a small metal tank at an original pressure of 32.6 lb/in<sup>2</sup>. This gave an initial tritium activity in the tank of 0.25 mc per standard  $\text{cm}^3$ . Samples of this mixture were taken over a period of nine months, and appropriate corrections were made for the decay of the tritium activity. The original mole ratio of tritium to hydrogen in this gas was  $1.38 \times 10^{-4}$ . However, the two slowly reacted to form tritium hydride so that this figure, when corrected for radioactive decay, actually represented the ratio of tritium plus tritium hydride to hydrogen.

A similar dilution of tritium was made with helium gas in place of hydrogen so that no tritium hydride could be formed.

Samples from the tritium-hydrogen or tritium-helium reserve tanks were introduced into the carrier gas by means of a by-pass cell of 4.43  $\text{cm}^3$  volume. This by-pass cell could be evacuated and then filled to any desired pressure, after which the carrier gas was diverted through it before reaching the chromatographic column.

## Experimental results and conclusions

*Palladium on flint-quartz column.* It was found by THOMAS and SMITH [2] that partial resolution of hydrogen-deuterium mixtures by gas-elution chromatography in a column containing palladium black supported on flint quartz could be effected. An extension of this elution technique was made to hydrogen-tritium mixtures.

Samples of hydrogen-tritium mixtures up to a total pressure of 500 mm were eluted through the column with argon as the carrier gas and column temperatures of 150–175°C. No apparent activity in the form of either tritium or tritium hydride was eluted from the column at these temperatures. This was attributed to the strong absorptive properties of the palladium metal for hydrogen, to the length of the column employed and to the very small amounts of tritium and tritium hydride present. When the column temperature was slowly raised to 300°C under carrier flow, a small amount of activity was observed on the electrometer, but no apparent separation of components was observed. The activity detected at these elevated temperatures should be eluted from the column in the form of tritium, since the palladium metal effectively catalyzes the hydrogen-tritium: tritium hydride conversion. Results of this work indicate that tritium is more strongly absorbed by the palladium metal than is hydrogen; hence, the method could be used to concentrate

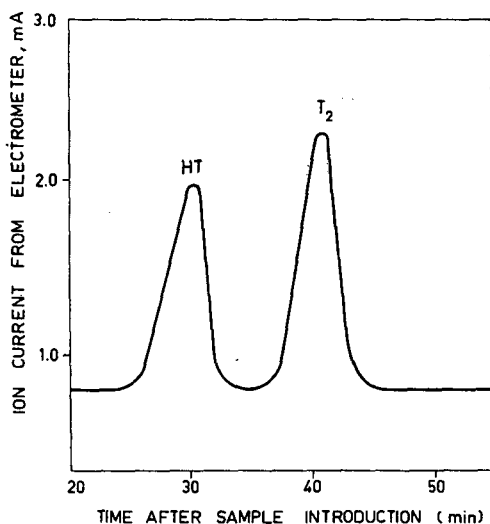


Fig. 1

Typical electrometer recorder trace for  $H_2$ -HT- $T_2$  sample (394.4 mm, 4.43 cc, 25°C) with hydrogen carrier at a flow rate of 65 cc/min through 25-ft silica gel (40–60 mesh) column at 77°K.

tritium from hydrogen samples but would not be effective in the absolute resolution of hydrogen-tritium: tritium hydride mixtures in accordance with the results obtained by CHADWICK [10].

*Silica gel column.* Silica gel has been found effective in the separation of hydrogen deuteride and deuterium at the temperature of liquid nitrogen with hydrogen as the carrier gas. Partial resolution of hydrogen, hydrogen deuteride and deuterium has also been observed at the temperature of boiling methane with helium as carrier

[7]. Experiments were performed with both of these carriers at 77 °K. Helium failed to elute hydrogen, tritium hydride or tritium; but hydrogen gave excellent resolution of the tritium hydride and tritium. The results are shown in Fig. 1. It should be noted that, since a tritium hydride molecule has only one-half the activity of a tritium molecule, the peak area of the former should be doubled for comparison of quantities of the two gases.

*Chromia on alumina column.* Activated alumina coated with chromia ( $\text{Cr} + \text{Cr}_2\text{O}_3$ ) was found to be effective in the separation of hydrogen, tritium hydride and tritium at 77 °K with both helium and neon as the carrier gas. The chromia-alumina column was deactivated with distilled water and partially reactivated at 150 °C under a low helium flow rate for a period of 12 h. The state of column activation is quite critical in the production of effective resolution of hydrogen, tritium and tritium hydride. At reactivation temperatures greater than 160 °C the isotope separation remains good, but the retention times for the components in the equilibrium mixture become prolonged; and, as a result, the peaks observed from ionization chamber response to tritium hydride and tritium activity become considerably broadened. At reactivation temperatures less than 145 °C resolution of the isotopic species becomes less pronounced even though the peaks observed are sharp and essentially symmetrical. The optimum column reactivation temperature producing effective component resolution, sharp and symmetrical elution peaks and reasonable elution times has been found to be approximately 150 °C. A typical combined electrometer recorder and katharometer recorder trace, employing identical recorder chart speeds so that the time axes are identical, for the elution of a sample

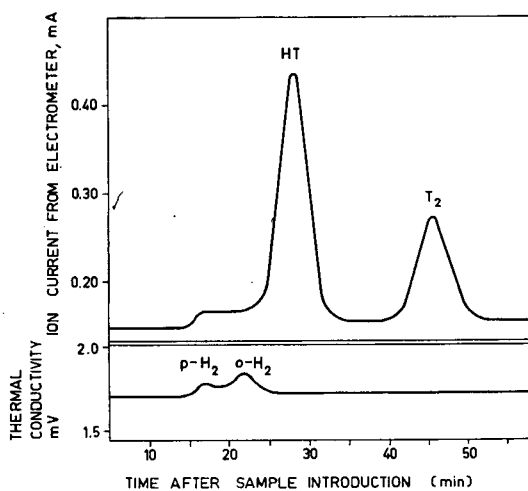


Fig. 2

Typical synchronized electrometer and katharometer recorder traces for  $\text{H}_2$ -HT- $\text{T}_2$  sample (371.8 mm, 4.43 cc, 25 °C) with helium carrier at a flow rate of 65 cc/min through partially deactivated (water, 150 °C) chromia-alumina (40–60 mesh) column at 77 °K.

mixture of hydrogen, tritium and tritium hydride at known pressure and volume is shown in Fig. 2. An ionization chamber polarization potential of  $-225$  V, a sensitivity setting of 1 V full scale on the electrometer and the  $10^{10}$ - $\Omega$  leak resistor were employed to obtain a series of curves essentially identical with that given in

Fig. 2. The katharometer employed thermistor detector elements and was set at maximum sensitivity.

Examination of Fig. 2 indicates that column deactivation is apparently sufficient to allow partial resolution of para- and orthohydrogen spin isomers while still it is active enough to allow complete resolution of tritium and tritium hydride. Subsequent column poisoning followed by reactivation at 140°C yielded the typical elution curves shown in Fig. 3. Resolution of tritium hydride and tritium became

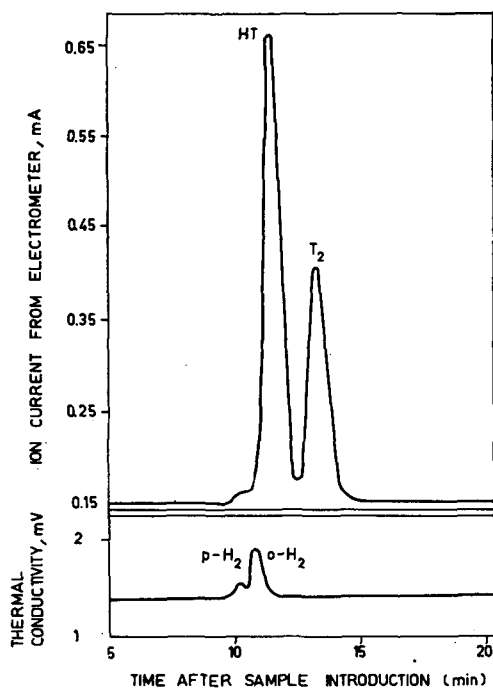


Fig. 3

Typical synchronized electrometer and katharometer recorder traces for H<sub>2</sub>-HT-T<sub>2</sub> sample (332 mm, 4.43 cc, 25°C) with helium carrier at a flow rate of 80 cc/min through partially deactivated (water, 140°C) chromia-alumina (40–60 mesh) column at 77°K.

less effective, while the orthohydrogen-parahydrogen resolution became slightly better, as expected. It will be noticed that there is partial overlap of the orthohydrogen and tritium hydride peaks, indicating that the column in its deactivated state does not effectively separate orthohydrogen and tritium hydride. It will also be noted that there is a shoulder on the electrometer trace corresponding to the elution of hydrogen. This is caused by a change in the leak rate in the electrometer as the sample enters the chamber. The effect of increased flow rate of the carrier on peak shapes, elution times and effective resolution of components is also shown in Fig. 3. The orthohydrogen-parahydrogen elution order and ortho- to parahydrogen ratio of approximately 2.8 to 1.2 in the samples employed indicate that the paramagnetic character of the chromia leading to orthohydrogen-parahydrogen conversion on the column is considerably reduced by poisoning with distilled water followed by low temperature reactivation. The results obtained with this partially poisoned column

with regard to orthohydrogen-parahydrogen resolution are in good agreement with the results obtained by VAN HOOK and EMMETT [4], who employed helium and neon carriers over activated alumina at 77 °K.

In an effort to enlarge the hydrogen peaks, which are relatively small when helium is used as the carrier gas, neon was employed under conditions identical with those given in Fig. 2. A series of samples was run, and typical simultaneous electrometer and katharometer traces are given in Fig. 4. Excellent resolution of tritium,

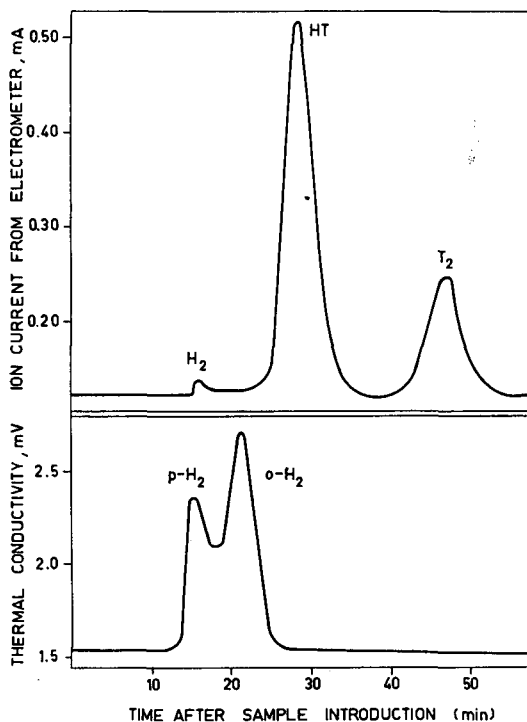


Fig. 4

Typical synchronized electrometer and katharometer recorder traces for  $H_2$ -HT- $T_2$  sample (211 mm, 4.43 cc, 25 °C) with neon carrier at a flow rate of 62 cc/min through partially deactivated (water, 150 °C) chromia-alumina (40–60 mesh) column at 77 °K.

tritium hydride and hydrogen was obtained with neon carrier in reasonably short elution times. At higher column reactivation temperatures the orthohydrogen-parahydrogen conversion was slightly more pronounced. Absolute resolution of hydrogen spin isomers has, as yet, not been achieved. These data are also in good agreement with those of VAN HOOK and EMMETT [4].

An analytical method for the accurate determination of tritium and tritium hydride content (% composition and activity in mc) in sample mixtures of hydrogen, tritium and tritium hydride at various total pressures, with the 8-ft chromia-alumina column with helium carrier at 77 °K, was developed.

A glass ampoule of 0.89 cm<sup>3</sup> volume containing 1 c of tritium at 475 mm pressure was expanded into a 1550 cm<sup>3</sup> volume tank and diluted with helium to a total pressure of 32.8 lb/in<sup>2</sup>. The ratio of helium pressure to tritium pressure in the tank was

therefore  $7.094 \times 10^3$ . Thus, in any given total pressure sample of helium and tritium, the tritium pressure is calculable. A series of various pressure samples of helium and tritium were run through the column, and a plot was made of tritium *peak area* (peak height times the width at one-half peak height) versus the pressure of tritium in the sample. From the linear relationship obtained the pressure of tritium in a sample mixture of hydrogen, tritium and tritium hydride, prepared by dilution of tritium (1 c, 0.89 cm<sup>3</sup>, 25 °C, 475 mm) with hydrogen to approximately the same ratio as in the helium dilution, could be calculated.

The initial dilution ratio of hydrogen to tritium in the absence of equilibration ( $H_2 + T_2 \rightleftharpoons 2HT$ ) in the hydrogen dilution tank was similarly calculated. This ratio ( $P_{H_2}/P_{T_2}$ ) was  $6.15 \times 10^3$ . Essentially 100% conversion of tritium to tritium hydride in various pressure samples from this tank was obtained by equilibration of the mixture over a hot (1200 °C) nichrome wire in a 100 cc volume exchange cell. The ratio of hydrogen pressure to tritium hydride pressure in these samples was therefore  $3.073 \times 10^3$ . A series of samples of this equilibrated mixture, at various total pressures, was eluted through the column with helium carrier; and a linear plot of tritium hydride peak area versus tritium hydride pressure in the sample was constructed. From such a plot the pressure of tritium hydride in an unknown mixture of hydrogen, tritium and tritium hydride can be obtained. The hydrogen pressure in a sample is obtained by the difference in the total sample pressure and the total tritium hydride and tritium pressure. Sample volumes were constant; hence, all sample pressures were converted to 25 °C. The results obtained by this method, on the chromia-alumina column, for mixtures of hydrogen, tritium and tritium hydride taken from the hydrogen dilution reservoir at a time interval between samples of about 7 d, are given in Table I. The data given show the slow progress

TABLE I  
ISOTOPIC COMPOSITION FOR MIXTURES OF HYDROGEN ISOTOPES  
AT 25 °C AS DETERMINED BY GAS CHROMATOGRAPHY

P Sample (mm of Hg)	Partial Pressures (mm of Hg)			Composition		
	$P_H$	$P_{T_2}$ ( $\times 10^2$ )	$P_{HT}$ ( $\times 10^2$ )	$H_2$ (%)	$T_2$ (%)	HT (%)
371.8	371.66	4.58	8.90	99.962	0.0123	0.024
385.2	385.07	3.88	9.25	99.966	0.0101	0.024
332.0	331.89	2.68	8.80	99.966	0.0080	0.0265
286.9	286.80	2.19	7.75	99.965	0.0076	0.0270

towards the establishment of equilibrium in the reservoir over a period of time. The equilibrium constant for the isotopic reaction ( $H_2 + T_2 \rightleftharpoons 2HT$ ) at 25 °C was calculated from thermodynamic partition functions and found to be approximately 2.5. From the initial hydrogen and tritium pressure in the reservoir, the percentage compositions of the isotopic species at equilibrium were calculated and found to be  $H_2$ —99.967;  $T_2$ — $3.4 \times 10^{-6}$ ;  $HT$ —0.0325. The data given in Table I agree quite well with trends toward these equilibrium values. Experimentally determined pressures for the active components (tritium and tritium hydride) in a series of samples were converted to the corresponding total reservoir volume pressures; and, since the initial pressure of tritium in the reservoir was known to correspond to 1 c activity (accounting for approximately 7.54%  $T_2$  decay over the time interval since initial dilution), the activities of the tritium hydride and tritium components in the

isotopic mixture were calculated and found to range from 0–120  $\mu\text{c}$  ( $\text{H}_2^3$ ) per cc of sample gas, depending on the sample pressure employed.

*Ferric oxide on alumina column.* Activated alumina (80–100 mesh) coated with ferric oxide was also found to be effective in the separation of hydrogen, tritium hydride and tritium at 77°K with helium as the carrier gas. The ferric oxide on alumina column was initially activated by heating at 200°C under flowing nitrogen for a period of 12 h. It was deactivated in a manner analogous to that employed with the chromia-alumina column. Optimum column reactivation temperatures, leading to the most effective resolution of the three isotopic species, were found to be in the range 130–140°C. This effective temperature range is slightly lower than it is in the case of the chromia-alumina column. A typical electrometer recorder and katharometer recorder trace for the elution of a mixture of hydrogen, tritium and tritium hydride is shown in Fig. 5. It is interesting to note that in this case

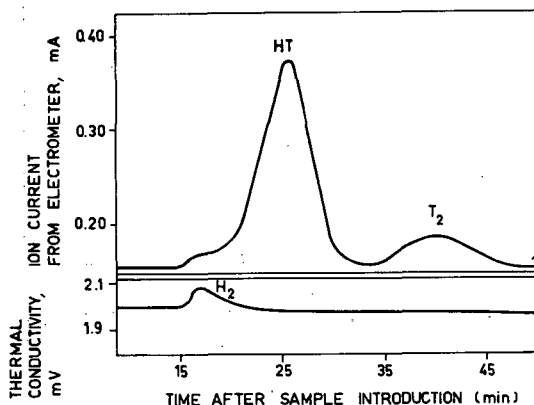


Fig. 5

Typical synchronized electrometer and katharometer recorder traces for  $\text{H}_2$ -HT- $\text{T}_2$  sample (415.2 mm, 4.43 cc, 25°C) with helium carrier at a flow rate of 60 cc/min through partially deactivated (water, 140°C) ferric oxide on alumina (80–100 mesh) column at 77°K.

the ortho- to parahydrogen conversion in the column, catalyzed by the paramagnetic ferric oxide, retarded separation of these spin isomers. The leading parahydrogen was partially converted to orthohydrogen, and the slower moving orthohydrogen was partially converted to parahydrogen. This tends to sharpen the hydrogen peak. The breadth of the hydrogen trace in Fig. 5 indicates that, although two peaks are not evident, only partial equilibration between the spin isomers was obtained.

*Alumina column.* An 8-ft column of unactivated alumina (80–100 mesh) at 77°K gave no separation of tritium and tritium hydride with helium as a carrier. This column was activated at 370°C under flowing helium for a period of 8 h. After such activation, the column proved to be exceedingly effective at 77°K in the resolution of hydrogen, tritium hydride and tritium when helium was employed as a carrier. This result was somewhat unexpected, since such a column was found by SMITH and HUNT [6, 7] to be relatively ineffective in the separation of hydrogen, hydrogen deuteride and deuterium. The results are shown in Fig. 6. It is interesting to note that the change in leak rate in the electrometer chamber caused by the presence of hydrogen itself in the helium was sufficient to show the complete separation of hydrogen from the other components of the sample.

In conclusion, it was demonstrated that hydrogen, tritium hydride and tritium

can be separated by gas chromatography even when the tritium is present in tracer quantities only and that the method can be applied to the analysis of such a mixture as well as to the concentration of the radioactive isotope.

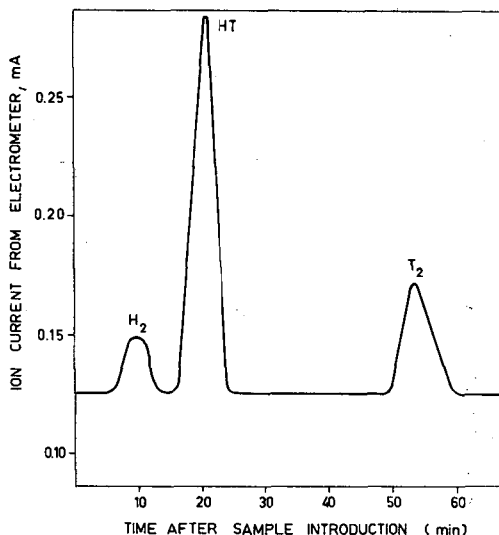


Fig. 6

Typical electrometer recorder trace for  $H_2$ -HT- $T_2$  sample (343 mm, 4.43 cc, 25°C) with helium carrier at a flow rate of 65 cc/min through 8-ft activated alumina (80–100 mesh) column at 77°K.

### ACKNOWLEDGEMENT

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### DISCUSSION X

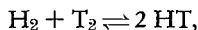
J. G. Burr (United States of America): Using the following percentage composition figures from Table I in the paper:  $H_2$  — 99.96;  $T_2$  — 0.0123; HT — 0.0240,



we find that  $(T) = 0.06 \text{ ml}/100 \text{ ml} - 0.15 \text{ c}/100 \text{ ml}$ . This  $(T)$  corresponds to a dose rate of 5 keV electrons of

$$\frac{0.15 \times 4 \times 5 \times 10^{10} \text{ d} \times 10^3 \text{ eV}}{100 \text{ ml sec.}} = \frac{3 \times 10^{10} \text{ eV}}{\text{ml sec.}}$$

If for the exchange the  $G = 10\,000$



then  $\frac{3 \times 10^{12} \text{ mol.}}{\text{ml sec.}}$  are exchanging and the exchange should be nearly complete in

about 100 d, i. e. the HT/T<sub>2</sub> peak ratio should increase at about 1—2% d. Was any such growth of HT observed?

**H. A. Smith** (United States of America): An examination of Table I shows that the HT/T<sub>2</sub> ratio changed from approximately 2.0 to 3.5 in about 21 d. The analytical method has not been worked out in sufficient detail to give more exact answers.

**J. G. Burr**: I should also like to ask what caused the peak for hydrogen.

**H. A. Smith**: We believe — although this is only speculation — that it was caused by a change in the leak rate through the gas in the chamber. As you know, there is a normal leak rate due to the presence of cosmic rays which cause ion pairs, and this depends upon the nature of the gas in the chamber.

**E. Roth** (France): We have been working for some time on the same analytical problems as Prof. Smith. I might add that we have found that hydrogen itself is a very satisfactory carrier for HT, HD and D<sub>2</sub> and we even have a small peak of H<sub>2</sub> in hydrogen, due to the fact that there is a difference between the absorption of ortho- and parahydrogen on the column itself. Similar work has been reported earlier by Russian authors who, I believe, also used hydrogen.

**H. A. Smith**: I would recall, in this connection, that in my first slide (Fig. 1) I showed that we had used hydrogen as a carrier on silica and had obtained very good separation of HT and T<sub>2</sub>.

**H. S. Isbel** (United States of America): Did Prof. Smith check experimentally whether hydrogen passed through his apparatus without any tritium could cause the hypothetical increase in leak rate in the vibrating reed ascribed to hydrogen and also whether the effect might be caused by a memory effect arising from the high-activity tritium that had been passed through the ion chamber immediately before the hydrogen?

**H. A. Smith**: The answer is: Yes. We prepared a brand new column which had never been exposed to tritium (so that no memory effect could have been involved). The resulting traces were obtained from a sample of pure hydrogen with helium as a carrier at 77°K. The thermal conductivity trace (see below) indicates the hydrogen clearly, with partial separation into two peaks. These are caused by the presence of the nuclear spin isomers, parahydrogen and orthohydrogen. The electrometer trace (see below), which is synchronized with the thermal conductivity trace, not only shows clearly the change of ion current with the passage of the hydrogen sample, but also indicates the partial separation of the nuclear spin isomers.

**J. R. Gat** (Israel): Could Prof. Smith comment on the applicability — for purposes of measurement — of the gas chromatographic method for pre-enrichment of tritium at a natural level of activity?

**H. A. Smith**: We have not attempted any pre-enrichment of tritium at a natural level of activity; however, there may well be an application of the chromato-

graphic method to the problem of tritium determination in natural waters. When the natural water samples are concentrated by electrolysis, high percentages of deuterium are obtained, and these can be evaluated quantitatively by gas chromatography. It may be possible to refine the detection system so that the deuterium and tritium may be determined simultaneously on a very small sample of the residue from electrolysis.

**B. Gonsior** (Federal Republic of Germany): I should like to comment upon the use of a thermal diffusion column capable of continuous operation for concentrating tritium. The fundamental equation of thermodiffusion (1—5) applied to a mixture of  $H_2 + HT$  lead to the dimensions of the plant given in Table I.

TABLE I  
DIMENSIONS AND NORMAL PERFORMANCE CONDITIONS

Radius of the wire	0.025 cm
Radius of the tube	1—2 cm
Temperature of the wire	500 °C
Temperature of the cold wall	20 °C
Amount of gas-flow	0.5 cm <sup>3</sup> sec <sup>-1</sup>
Derichment	100
Length of derichment column	440 cm
Enrichment	1000
Length of enrichment column	360 cm

The experimental arrangement is shown in Fig. 1. The apparatus consists of four stages which are convectively coupled. Two of these stages form the "derichment column" while the other two stages comprise the "enrichment column", the last stage of which may be isolated by stopcocks so that the hydrogen may be withdrawn. The mixture which it is required to enrich in tritium is introduced in the apparatus between the derichment and enrichment columns. A pipe from the end

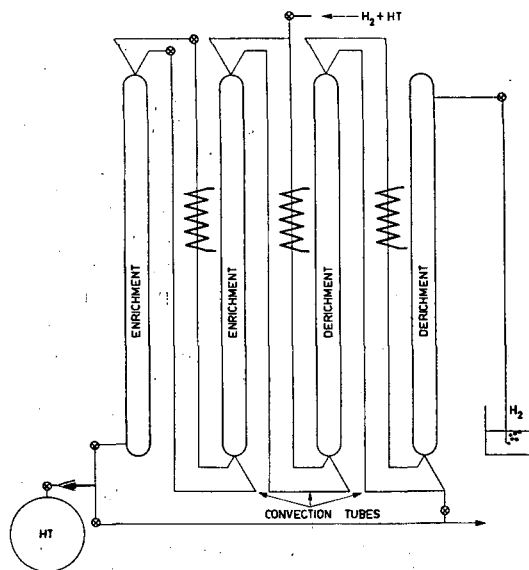


Fig. 1

of the "derichment column" leads into an organic oil to prevent air entering the apparatus. During continuous operation the outgoing hydrogen from the "derichment column" contains not more than 1% of the incoming concentration. The volume of the whole apparatus is 12 l while that of the last enrichment stage is 1.5 l.

The performance of the apparatus was examined by introducing a known quantity of tritium, running the apparatus for some hours, and then measuring the percentage of tritium in the final enrichment stage. The apparatus was filled with tritiated hydrogen at pressures varying between 25 and 75 cm of mercury and at temperatures of 400 and 500 °C. The results are shown in Fig. 2, from which it is seen that an efficiency of 100% was obtained after 15 h operation at 500 °C and at a pressure of 70 cm mercury. Equilibrium of 100% was obtained.

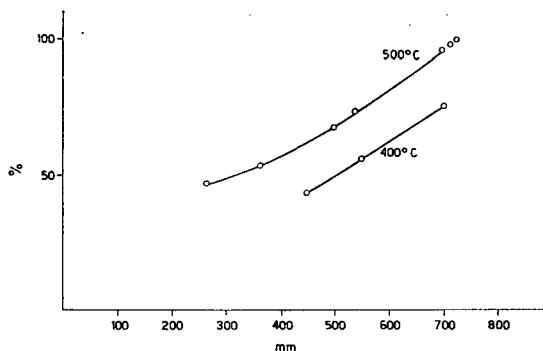


Fig. 2

Using this method it is possible to enrich samples having a low concentration of tritium. It is not necessary to know the separation factor for tritium since the apparatus may be so constructed that the tritium may be quantitatively extracted and measured.

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B

TRITIUM IN CHEMISTRY AND PHYSICS

(Session II)



# ISOTOPE EFFECTS ACCOMPANYING USE OF TRITIUM AND DEUTERIUM IN THE STUDY OF ORGANIC RADIATION CHEMISTRY

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Abstract — Résumé — Аннотация — Resumen

**Isotope effects accompanying use of tritium and deuterium in the study of organic radiation chemistry.** The subject of the paper is the types of isotope effects which must be considered in using tritium and deuterium to study the radiolysis of organic compounds. Overall isotope effects are defined for several types of labelling such as the use of partially-labelled materials (where the labelling is either random or specific) and mixtures of wholly-labelled with wholly-unlabelled substrates. Contributions to the overall isotope effect are analysed in terms of (1) isotope effects in excitation processes; (2) isotope effects in the dissociation of excited molecules; and (3) isotope effects in the secondary radical reactions. The quasiequilibrium theory of molecule-ion dissociation is used to estimate quantitatively the isotope effects accompanying loss of hydrogen and deuterium atoms from biphenyl molecule-ions; this application is discussed. It is shown how scavenger techniques can be used to estimate the isotope effect accompanying loss of hydrogen and deuterium by non-radical processes in the radiolysis of deuteriated methanols. Existing literature about isotope effects in the secondary radical reactions is summarized critically. The existence of pronounced secondary isotope effects in the formation and reactions of deuterated aliphatic radicals is emphasized.

**Effets isotopiques accompagnant l'emploi du tritium et du deutérium dans les recherches en radiochimie organique.** Le mémoire est consacré aux effets isotopiques dont il faut tenir compte en utilisant le tritium et le deutérium dans l'étude de la radiolyse de composés organiques. L'auteur définit les effets isotopiques globaux pour plusieurs procédés de marquage, tels que l'emploi de matières partiellement marquées (marquage aléatoire ou spécifique) ou de mélanges de substrats entièrement marqués et non marqués. Les éléments de l'effet isotopique global sont analysés en tenant compte: (1) des effets isotopiques au cours des processus d'excitation; (2) des effets isotopiques durant la dissociation des molécules excitées; (3) des effets isotopiques lors des réactions secondaires entre radicaux. On applique la théorie du quasi-équilibre de la dissociation molécules-ions pour évaluer quantitativement les effets isotopiques qui accompagnent la perte d'atomes d'hydrogène et de deutérium du biphenyle en équilibre molécules-ions; ce procédé fait l'objet d'un examen critique. L'auteur montre comment on peut utiliser les méthodes de balayage pour évaluer l'effet isotopique qui accompagne la perte d'hydrogène et de deutérium par suite de processus sans intervention de radicaux qui s'opèrent pendant la radiolyse des méthanols deutérés. Le mémoire contient un bref exposé critique des travaux publiés sur les effets isotopiques dans les réactions secondaires en présence de radicaux. Il met en lumière la présence d'effets isotopiques secondaires marqués lors de la formation des radicaux aliphatiques deutérés et de leurs réactions.

**Изотопические эффекты, сопровождающие использование трития и дейтерия в радиационной химии органических веществ.** В работе дается описание изотопических эффектов, которые следует учитывать при использовании трития и дейтерия для изучения радиолитического распада органических соединений. Определяются общие изотопические эффекты для отдельных видов мечения, таких, как использование частично меченых материалов (когда мечение либо беспорядочно, либо специфично) и смесей полностью меченых субстратов с полностью намеченными субстратами. Общий изотопический эффект анализируется по его составным частям, а именно: 1) изотопические эффекты при процессах возбуждения; 2) изотопические эффекты

при диссоциации возбужденных молекул; и 3) изотопические эффекты при побочных реакциях радикалов. Теория квазиравновесия диссоциации молекула-ион используется для количественного определения изотопических эффектов, сопровождающих потерю атомов водорода и дейтерия у дифениловых молекул-ионов; обсуждается применение этой теории. В работе показываются, как методы акцептора радикалов могут использоваться для оценки изотопического эффекта, сопровождающего потерю водорода и дейтерия при нерадикальных процессах в радиоллизе насыщенных дейтерием метанолов. Дается критическая оценка имеющейся литературе по изотопическим эффектам при побочных реакциях радикалов. Подчеркивается существование резко выраженных побочных изотопических эффектов при образовании и реакциях насыщенных дейтерием алифатических радиокальв.

**Efectos isotópicos que se producen al emplear tritio y deuterio en el estudio de la radiólisis de sustancias orgánicas.** La memoria trata de los tipos de efectos isotópicos que es preciso tener en cuenta al estudiar con ayuda de tritio o de deuterio la radiólisis de compuestos orgánicos. Define los efectos isotópicos globales correspondientes a marcaciones de varias índoles, como el empleo de sustancias parcialmente marcadas (tanto aleatoria como específicamente) o de mezclas de sustancias totalmente marcadas con sustratos enteramente no marcados. El efecto global se analiza según lo que a él contribuyen 1) los efectos isotópicos en procesos de excitación, 2) los efectos isotópicos en la disociación de moléculas excitadas y 3) los efectos isotópicos en las reacciones secundarias de radicales. El autor examina la posibilidad de recurrir a la teoría del cuasiequilibrio de la disociación de los iones moleculares para evaluar cuantitativamente los efectos isotópicos que acompañan a la pérdida de átomos de hidrógeno y de deuterio por iones moleculares difenilo. También demuestra de qué manera pueden servir las técnicas que emplean depuradores para calcular el efecto isotópico que, en la radiólisis de metanoles deuterados, acompaña a la pérdida de hidrógeno y deuterio en virtud de procesos en que no intervienen radicales. El autor analiza críticamente la bibliografía existente sobre los efectos isotópicos en reacciones secundarias de radicales. Destaca la intervención de efectos isotópicos secundarios muy pronunciados en la formación y en las reacciones de radicales alifáticos deuterados.

## Introduction

The action of ionizing radiation on organic materials produces hydrogen gas as a major product. This product results naturally from unimolecular dissociation of whatever carbon-hydrogen bonds are present in the molecule and from various types of bimolecular processes, such as the interaction between a hydrogen atom and the organic molecule. Hydrogen is also product formed by absorption in organic substances of ultraviolet light in the short wave-length regions (xenon resonance radiation, for example), or by mercury-photosensitized reactions in the medium ultraviolet wave-length regions.

Knowledge of the reaction steps and rate processes concerned in the formation of a major product such as hydrogen can be expected, generally, to provide a good insight into the nature of the over-all decomposition of the molecule; thus, the formation of radiolytic hydrogen from organic molecules has been the subject of many investigations [2]. The most effective tool for these investigations has been the use of isotopic hydrogen tracer techniques [3] and hydrogen atom scavengers [4] or a combination of these two techniques. Since the isotopic hydrogen tracers necessarily used for these investigations are hydrogen, deuterium and tritium, where the difference in masses and the difference in zero-point vibrational energy of bonds with these isotopes are large, the potential isotope effect on rates, exchange reactions and equilibria are large; these isotope effects



have greatly complicated the interpretation of the results of the experiments. The complications are particularly severe because the isotope effects in the dissociation of electronically excited molecules, and in many of the particular bimolecular secondary reactions, have never been quantitatively considered or discussed, except in the most cursory fashion. This lack of information is in decided contrast with the relatively thorough understanding of most kinetic isotope effects [5] for reactions involving only vibrationally excited molecules or the interactions of species with only thermal kinetic energies.

Isotope effects in the dissociation reactions of electronically excited molecules should occur not only in the dissociation of carbon-hydrogen bonds but also, as will be emphasized below, in the dissociation of carbon-carbon, and other bonds, in molecules which contain a substantial fraction of carbon-tritium or carbon-deuterium bonds. Surprisingly enough, this sort of secondary isotope effect has not been considered in photochemical studies where dissociation of deuterium-labelled molecules, such as ketones, are very commonly involved although primary isotope effects in radical abstraction reactions have proved a great source of information on mechanisms [6]. Only for dissociations of the molecule-ions formed in the mass spectrometer has consideration of both the primary and the secondary isotope effects been explicitly considered [7].

It is the principal purpose of this paper to discuss the types of isotope effects which must be considered in the use of tritium to study the formation of hydrogen in the radiolysis of organic compounds, to report what few examples of information on these effects exist in the literature and to present the theory which must be applied in the case of isotope effects accompanying the dissociation of electronically-labelled organic molecules containing tritium. Many of the examples discussed here will necessarily be drawn from experiments where deuterium-labelled molecules rather than tritium-labelled molecules were used. It will be a secondary purpose of this paper to estimate the usefulness of this deuterium data for predictions of magnitudes and direction of tritium isotope effects.

### A. The overall isotope effect

This, the most obviously measurable isotope effect, can be measured in several different ways. For example, if one considers hydrogen and deuterium formed in the radiolysis of a series of partially and selectively deuterated biphenyls [8], the over-all isotope effect can be measured as the yield of hydrogen,  $G(H_2)$ , from biphenyl relative to the yield of deuterium,  $G(D_2)$ , from biphenyl- $d_{10}$ . For the series of partially deuterated biphenyls a different sort of isotope effect can be calculated from the data: the specific yield of hydrogen (i. e.  $G(H_2) + 1/2G(HD)$ /number of C-H bonds in a molecule) relative to the corresponding specific deuterium yield from the *same substance*. For biphenyl and the deuterated biphenyls [8] the value of the first isotope effect,  $G(H_2)/G(D_2) = 3.08$ , was found to agree with the value of the second isotope effect,  $2.97 \pm 0.28$ . For organic molecules with different types of C-H and O-H bonds, such as ethanol [9] and acetic acid [9], or methanol (Table I) where the hydrogen originates in a highly selective manner from particular sets of hydrogen bonds, the whole concept of the overall isotope effect is superseded by another and more important consideration — the use of this tracer technique to indicate molecular specificity in the formation of hydrogen [3].

The above discussion is concerned with an over-all *intermolecular* isotope effect — i. e. the comparison of molecules in which all of a given type of hydrogen bond

is either hydrogen or deuterium. For tritiated molecules the corresponding situation would be the comparison of molecules where all of a given type of bond would be either hydrogen (or deuterium) or tritium. There are no examples of this in the

TABLE I  
THE RADIOLYSIS OF DEUTERATED METHANOLS WITH COBALT-60 GAMMA RAYS

Substance	$G$ (Hydro- gen)*	%H <sub>2</sub>	%HD	%D <sub>2</sub>	$G(\text{CH}_4)$	$G(\text{CO})$	Reference	Total dose 10 <sup>20</sup> eV/g
CH <sub>3</sub> OD	3.60±0.11	40.0	60.0	—	0.62***	—	This paper	3
CH <sub>3</sub> OD	—	36.0	60.0	4	—	—	††	—
CH <sub>3</sub> OD+4—5% D <sub>2</sub> O	4.25±0.06	32.4	65.0	2.5	0.34**	0.08	This paper	3
CD <sub>3</sub> OH	3.50±0.3	13.7	75.0	11.3	0.32†	—	This paper	3
CD <sub>3</sub> OD	4.09±0.04	0.0	3.7	96.3	0.04	—	This paper	3
CH <sub>3</sub> OH	5.32±0.14	—	—	—	—	—	—	—

\* By this, we mean  $G(\text{H}_2 + \text{HD} + \text{D}_2)$ .

\*\* Composition undetermined.

\*\*\* CH<sub>4</sub> = 86%; CH<sub>3</sub>D = 14%; CH<sub>4</sub>/CH<sub>3</sub>D = 6.

† CD<sub>3</sub>H/CD<sub>4</sub> = 0.46.

†† YIZUKA Y., OUCHI, Y., HIROTA, K. and KUSMOTO, G., *Nippon Kagaku Zasshi (J. chem. Soc. Japan)* (1957) 129; UCRL Translation 370).

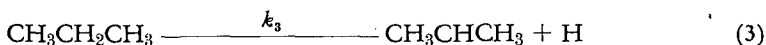
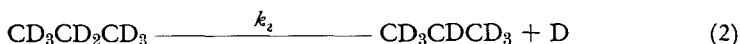
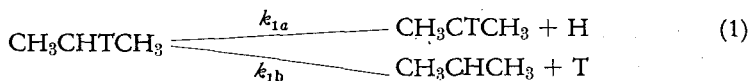
literature of radiation chemistry, and there are not likely to be any since a molecule containing such a high fraction of tritium would be subject to self-radiolysis at a very high rate (wholly tritiated ethane at atmospheric pressure, for example, would contain about 100 c of activity per 25 ml — with a half-thickness of only a few mm). Wholly tritiated molecules have been used to obtain data on vibrational structure and rotational structure of the molecules in question\*, but the radiation chemistry of such molecules has not been studied — except that STAATS, MORGAN and GOLDSTEIN report that their samples of TCN polymerized spontaneously in less than 12 h presumably because of self-radiolysis similar to that observed in compounds containing carbon-14 [11]. The decomposition of compounds such as benzene, toluene or ethane which contain an entire tritium atom, either randomly located or specifically located\* in a mass spectrometer (self-ionization) has been reported; but, of course, the process of beta decay which makes the ionized species detectable removes the tritium atoms and thus prevents observation of any isotope effect.

The few reported occasions on which a tritiated compound has been irradiated — acetic acid [13], toluene [14], methane [15] — have all involved organic compounds containing tracer amounts of tritium — i. e. only a small fraction of the hydrogen of a particular bond type or position has been replaced by tritium. The overall isotope effect which could be measured in this sort of experiment (although in the examples given no isotope effect in the formation of hydrogen was reported) would be an intramolecular isotope effect [16], shown as  $k_{1a}/k_{1b}$  in equation (1) for a hypothetical tritium-labelled propane, while the sort of isotope effect which has

\* For example, CT<sub>4</sub> has been prepared for use in the study of infrared spectra of methane, TCN and T<sub>2</sub>O; the various hydrogen species, H<sub>2</sub>, HD, D<sub>2</sub>, TH, TD and T<sub>2</sub> have been prepared and studied. [10]

\* WEXLER, ANDERSON and SINGE, for propane-t and the tritiated toluenes; WEXLER, for ethane-t; and CARLSON for benzene [12].

been reported for the deuterium compounds is the intermolecular isotope effect,  $k_2/k_3$ . Intermolecular and intramolecular isotope effects are



different in magnitude (for a reaction where each can be measured, such as the formation of carbon dioxide from  $\text{C}^{13}$ -labelled malonic acids) [17, 18]. Unfortunately, in each of the examples reported above [13, 14, 15] the tritium label was used to assist in measuring or identifying radiolysis products other than hydrogen-methane from acetic acid, methane and benzene from toluene, higher hydrocarbons from methane — and the use of this label to assist in mechanism determination for hydrogen formation or in measurement of overall tritium-hydrogen isotope effect has not yet been reported. A comparison of the inter- and intramolecular isotope effects would be very interesting.

The overall isotope effect for hydrogen formation in organic radiolysis is probably the result of isotope effects of varying magnitudes in each of the competitive and consecutive primary and secondary reactions which are intermediate in the formation of hydrogen. The nature and number of these intermediate processes is not entirely settled. In fact, the principal rationale for using tracers is to obtain more information about precisely this matter, and this is the principal information which can be gained from consideration of these isotope effects.

For the purposes of this discussion, component isotope effects can be considered under the following categories:

(1) Isotope effects in the ionization or excitation of isotopically labelled molecules. These appear to be absent or small\*, and it is likely that they simply reflect the small perturbation of the electronic transition probabilities by unsymmetrical vibrational modes. They will not be further discussed in this report.

(2) Isotope effects in the relative probabilities of dissociation and relative rates of dissociation of M-H, M-D and M-T bonds for electronically excited molecules (where M is usually C, O or N). This subject will provide a principal topic of this discussion.

(3) Isotope effects in the bimolecular reactions of electronically excited molecules with each other or with ground electronic state molecules. Very little is known about this matter, including the probability of such processes in liquid-state systems. It will not be discussed further here, except in passing.

(4) Isotope effects in the secondary reactions of H, D or T atoms. Existing knowledge on this matter will be briefly summarized; theoretical interpretation of such isotope effects is encompassed in well developed applications of existing reaction-rate theory [16, 17, 18] and will not be discussed here at length.

\* KRAUSS and KROPP report  $\Delta\text{IP}$  for  $\text{CH}_4$  and  $\text{CD}_4$  of 0.18 eV, however, and of 0.22 eV in  $\text{NH}_3$  and  $\text{ND}_3$  [18].

**B. Isotope effects in the reactions of H, D and T atoms with organic substances and in the reactions of organic radicals with  $H_2$ ,  $D_2$  and  $T_2$ .**

Pronounced isotope effects, both primary and secondary, do exist, and the data on these are extremely scanty and difficult to use.

The existence of primary isotope effects is apparent in the observed and calculated ratios of rate constants for the reactions of hydrogen and deuterium atoms with the corresponding molecules [19]:  $(H + H_2)/(D + D_2) = 1.93$ ;  $(H + H_2)/(D + H_2) = 1.12$ ;  $(H + D_2)/(D + D_2) = 1.07$ ;  $(H + H_2 = H_2)/(H + HD = H_2) = 2.98$ ;  $(D + D_2 = D_2)/(D + HD = D_2) = 1.42$ . A similar sort of primary isotope effect exists for the reaction of methyl radicals (and presumably for other organic radicals) with hydrogen and deuterium [20] since the ratios of rate constants for the following such reactions are reported:  $(CH_3 + H_2)/(CH_3 + D_2) = 3.3$ . The existence of an interesting secondary isotope effect is shown by the following ratio of rate constants:  $(CH_3 + H_2)/(CD_3 + H_2) = 0.71$ .

The corresponding isotope effect for the reactions of H and D atoms with organic molecules appears to have been almost completely ignored in the abundant literature reporting use of D atoms in the study of the reactions of "hydrogen" atoms with organic substances although it must certainly exist and be of measurable magnitude. These experiments have usually been carried out with D atoms for identification of a particular product of the reactions or as a study of the exchange reactions accompanying formation of the organic radicals. Broad general observations of this type are not invalidated or much altered by the existence of relatively small isotope effect in the atom reactions: thus, these isotope effects have rarely been specifically reported, and the measurements are not sufficiently accurate (since they are generally drawn from interpretation of data on free-radical reactions occurring in extremely complicated reaction schemes) to allow later estimate of the isotope effects. In plain fact, the workers in this field have used hydrogen or deuterium atoms almost at random and have discussed the results, the kinetics and the activation energies of both hydrogen and deuterium atom reactions as if the differences were insignificant. This situation arises in part because of the use of large amounts of hydrogen or deuterium, rendering unfeasible or impractical the measurement of isotope mixing in the hydrogen.

Information about the magnitude, and factors influencing the magnitude, of this isotope effect in H and D atom abstraction is essential for the estimation of the significance of the over-all isotope effect in radiolysis; the lack of this information is a distinct gap in the chemical literature. The principal information now available concerns the reactions of "hot" tritium atoms with  $H_2$  and  $D_2$  [21] and with deuterated isopropyl benzoate [22]. The tritium atoms resulted from the  $He^3$  (n, p.) T reaction. When they were formed in the presence of mixtures of  $H_2$  and  $D_2$ , the ratio HT/DT was found to be  $1.55 \pm 0.06$ . The T atoms reacted with hydrogens in the methyl group of the ester 1.41 times more rapidly than they did with deuterium atoms in the same methyl group; the preference for reaction with aryl ring hydrogen was 1.14 greater than it was for reaction with a ring deuterium. These data represent the only experimental study of the  $T + H_2 + D_2$  system. Since the rate-constant ratio for  $(H + H_2)/(H + D_2) = 1.8$ , and  $(D + H_2)/(D + D_2) = 1.7$  (all at  $1000^\circ C$ ), the corresponding value of the tritium atom rate ratio suggests that the reactions result from tritium atoms with kinetic energies equivalent to a temperature of  $1000^\circ C$ . The principal conclusion is that, considering over-all deuterium-isotope effects of 1.5–3.0<sup>3</sup>, the isotope effects in these abstraction reactions are large enough to be prominent contributors to the overall isotope effect. The data, how-

ever, are so scanty that even a semi-quantitative estimation of this contribution, or of the relative values of isotope effects in the several types of atom-molecule reactions, is out of the question. The rates of a number of these abstraction reactions of tritium atoms, particularly those with hydrogen and deuterium molecules, should be amenable to the theoretical calculations outlined by G. BOATO *et al.* [19] and derived from the semi-empirical treatment of L. FARKAS and E. WIGNER [23], particularly since many of the relevant properties of the isotopic hydrogen molecules have been tabulated [17, 18]. Comparison of the rate ratio for  $(T + H_2)/(T + D_2)$  for the mixture of species in thermodynamic equilibrium should prove a means for the estimation of the actual effective temperature of the recoil tritium atoms in ROWLAND's experiments [21].

### C. Hydrogen isotope effects in the dissociation of electronically excited molecules

Two types of dissociations will be discussed next: (1) dissociations which produce hydrogen atoms (from molecule-ions in the mass spectrometer, for example) and (2) dissociations which produce molecular hydrogen (and often another stable molecule, such as ethylene from ethane) without the detectable intervention of hydrogen atoms or other radicals. These sorts of process are variously called "molecular dissociations", "rearrangements" or "disproportionations".

Ordinary unimolecular reaction-rate theory [24] deals with molecules which have been vibrationally excited at a particular temperature and collision frequency by collision until the internal vibrational energy of a molecule exceeds some critical value for a particular reaction coordinate [25], or until the fraction of molecules with a total internal energy above a given threshold becomes large enough to produce a measurable amount of dissociation, according to the expression

$$k = Y \left[ \frac{E - E_0}{E} \right]^{n-1}. \quad (4)$$

Even the calculations of MARCUS [26] on the dissociation of excited methane molecules produced by recombination of hydrogen atoms with methyl radicals are probably concerned with molecules primarily vibrationally excited, since the energy of recombination is only about 4.4 eV; and the lowest detectable electronically excited state of methane is considerably higher than this.

Application of reaction-rate theory to electronically excited large molecules (such as produce the primary processes in photochemistry) does not appear to have been attempted, and dissociation of excited diatomic molecules has been evaluated by application of the Franck-Condon principle to molecules in which the potential energy surfaces are fairly well known. Dissociation of ionized diatomic molecules and a few three-atom molecules has also been discussed in a similar Franck-Condon manner [7], but the only existing treatment for dissociation of large organic molecule-ions is the quasi-equilibrium theory of mass spectra as exemplified in the original papers [27] and in some of the numerous applications and examinations of this theory [28-34].

The only direct experimental data for hydrogen isotope effects attending dissociation of electronically energized molecules are for dissociation of molecule-ions in the mass spectrometer, and much of the work along this line has not been devoted to the study of the isotope effects in these dissociations but simply to the use of deuterium labelling for identification of the ionic fragments which result from the dissociations [31]. The only references to the use of the quasi-equilibrium theory for estimation of the origin of these effects is in the original articles and in the study of propane- $d_2$  mass spectra [28], and this latter study suffers from some misunder-

standing of tracer applications. We would like to point out here that, in principle, the quasi-equilibrium theory should be applicable to dissociation of molecules excited to dissociative or predissociative electronic states, such as are encountered in photochemical studies. Since the understanding of singlet, triplet and pre-dissociative electronic states is considerably better than the understanding of ionized states — to the extent that quite precise knowledge of the excess internal energy in the excited molecules is possible — precise knowledge of some primary and secondary isotope effects in dissociation of these molecules could provide a better evaluation of the theory than could mass spectral data.

Recent studies in these laboratories of the loss of H and D atoms from the molecule-ions of biphenyl and deuterated biphenyls [32] have provided quite precise data on the primary and secondary isotope effects in these dissociations under the mass spectrometric conditions in that investigation. The data are briefly summarized in Table II, which is reproduced from *The Journal of Physical Chemistry*. The  $\Gamma$  fac-

TABLE II  
SPECIFIC PROBABILITIES FOR HYDROGEN AND DEUTERIUM LOSS

Compound	Loss of H or D			Loss of 2H + HD + 2D		
	$\Gamma_1$	$\Pi_1$	$IE = \Gamma_1/\Pi_1$	$\Gamma_2$	$\Pi_2$	$IE = \Gamma_2/\Pi_2$
Biphenyl (I)	1.00	(0.47)*	(2.12)*	1.00	—	—
Biphenyl-d <sub>2</sub> (II)	1.10	.56	1.91	1.07	0.47	2.30
Biphenyl-d <sub>4</sub> (III) and (IV)	1.18	.66	1.80	1.09	.62	1.76
Biphenyl-d <sub>6</sub> (V)	1.29	.73	1.72	1.12	.67	1.68
Biphenyl-d <sub>8</sub> (VI)	1.51	.79	1.91	1.42	.64	2.22
Biphenyl-d <sub>10</sub>	(1.48)*	.93	(1.59)*	(1.15)*	.74	(1.56)*

\* Values obtained by extrapolation.

tors shown in Table II are the specific losses of H, normalized to the same process in biphenyl; and the  $\pi$  factors are the similarly normalized specific losses of deuterium from those molecule-ions. It will be noted that the primary isotope effect is not the probability of H loss from biphenyl molecule-ion relative to the probability of D loss from biphenyl-d<sub>10</sub> molecule-ion; the relative probabilities of H and D loss must be compared in the same molecule-ion since these probabilities are obviously functions of the total hydrogen and deuterium contents of the molecule-ions.

The ratio of the  $\Gamma$  factor to the  $\pi$  factor was defined as the primary isotope effect, and the variation of both factors with the deuterium content of the molecule-ions was defined as a secondary isotope effect. The existence of both of these isotope effects was qualitatively discussed in terms of the quasi-equilibrium theory.

Extension of this theory to account for the relative probability of dissociation of a C-T bond, however, requires some quantitative application of the theory in a form in which parameters specific to C-H, C-D and C-T bonds appear. The following sections will present such a quantitative application; we shall be able to evaluate the factors which contribute to the primary and secondary isotope effects in dissociations of biphenyl molecule-ions and then estimate the primary isotope effect for the dissociation of hypothetical C-T bonds in such molecule-ions.

A very simple form of the quasi-equilibrium equation for rate constants will be employed for the calculation: equation (5), very similar to (4).

$$k = \nu_x \left[ \frac{\bar{E} - \epsilon_0}{\bar{E}} \right]^{3N-7} \quad (5)$$

We shall evaluate some of the parameters for application of this equation to biphenyl molecule-ions in the manner of W. A. CHUPKA [30].

The values of  $k$  which will permit simultaneous observation of parent and fragment ions fall within a very narrow range [30]. The fraction of parent ions in the biphenyl mass patterns (at 70 V, and 500 °K) [32] is 0.48 (for biphenyl-d<sub>10</sub> the value is 0.47). The geometry of mass spectrometers and the transit times of ions in this geometry are such that  $k$  must be very close to  $10^5$ ; we shall use  $1.0 \times 10^5$  (interpolation on Chupka's graph suggests  $8.0 \times 10^4$  as a better value, but this will vary from instrument to instrument). The values of the frequency factor,  $\nu_x$ , reflect among other things the change in entropy of activation from one reaction to another. D. P. STEVENSON [33] has produced a strong argument that, for dissociation of benzene molecule-ion according to (6), the value of  $\nu_H$  must be about  $10^{14}$ ; this is higher than the value of  $10^{12}$  used by L. FRIEDMAN *et al.* [35] for similar dissociation in some aliphatic alcohols.

In equation (5),  $\bar{E}$  represents the average internal energy content of the dissociating biphenyl molecule-ion; we shall estimate this by the method of Stevenson, equation (7):



$$f_p = \bar{E}'/2 \bar{E} \quad (7)$$

and shall use the difference between the appearance potentials for the processes,  $\text{C}_6\text{H}_6 = \text{C}_6\text{H}_6^+$ , and  $\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5^+ + \text{H}$  to approximate  $E'$  for the similar processes in biphenyl. We know the appearance potentials for biphenyl molecule-ion, 8.84 [34], but we do not know the appearance potential of  $\text{C}_{12}\text{H}_9^+$ . From these values for biphenyl;  $f_p + 0.48$  and  $E' = 5.16$  (7), the value of  $E = 5.53$ .

We shall now obtain the value of the threshold energy for the dissociation process,  $e_0$ , by using the above parameters and equation (5) to give (8):

$$1.0 \times 10^5 = 10^{14} [(5.53 - e_0)/5.53]^{59} \quad (8)$$

whence  $e_0 = 1.64$ .

The parameters by means of which we can now introduce consideration of the differing effects of C-H, C-D and C-T bonds upon the value of the rate constant will be the difference in zero point energies and the differences in non-fixed energies [27, 32], where these differences are computed by equations (9) and (10).

$$A = \frac{1}{2} b (\nu_{\text{CX}} - \nu_{\text{CH}}) \quad (9)$$

$$B = \frac{b\nu_{\text{CH}}}{\exp(b\nu_{\text{CH}}/kT) - 1} - \frac{b\nu_{\text{CX}}}{\exp(b\nu_{\text{CX}}/kT) - 1} \quad (10)$$

These parameters will be inserted into the rate equation according to (11):

$$k = \nu_{\text{CX}} \left[ \frac{\bar{E} - e_0 + nB - A}{E + B} \right] \quad (11)$$

A will be used in the equation only when  $\nu_{\text{CX}}$  refers to dissociation of a C-X bond (where X is D or T); B represents the change in nonfixed energy of the molecule-ion when a C-H bond is replaced by a C-X bond and thus will enter the equation with a coefficient,  $n$ , where  $n$  is the number of C-X bonds in the particular biphenyl molecule-ion. The value of the frequency constant is so approximate that

it is difficult to justify variation of this with the nature of the bond being ruptured; but, according to A. KROPF *et al.* [28] it could be entered with a coefficient which is 0.7 for C-D bond dissociation and 0.58 for C-T bond dissociation. The effect of this variation will be illustrated below.

Values for the C-X stretching frequencies which become the translational mode in the transition state were taken from the known spectra of biphenyl and biphenyl-d<sub>10</sub> [38],  $\nu_{\text{CH}} = 3060 \text{ cm}^{-1}$  ( $9.18 \times 10^{13} \text{ sec}^{-1}$ ,  $6.06 \times 10^{-13} \text{ ergs}$ ),  $\nu_{\text{C-D}} = 2280 \text{ cm}^{-1}$  ( $6.84 \times 10^{13}$ ,  $4.51 \times 10^{-13} \text{ ergs}$ );  $\nu_{\text{C-T}}$  was taken as  $\nu_{\text{C-H}} (1/\sqrt{3})$  or  $1920 \text{ cm}^{-1}$  ( $5.71 \times 10^{13} \text{ sec}^{-1}$ ,  $3.78 \times 10^{-13} \text{ erg}$ ). With these values  $A$  then becomes 0.048 eV for rupture of a C-D bond, and 0.0712 eV for rupture of a C-T bond.  $B$  has a numerical value of 0.00096 eV for each C-D bond in the biphenyl molecule and of 0.0023 eV for each C-T bond.

Using these numerical values, we can now calculate the variation in  $k$  as a function of the number of C-D or C-T bonds in the molecule, and for the probability of C-D bond rupture and C-T bond rupture relative to C-H bond rupture. The calculations will provide a measure of whether variation in the  $A$  factor is sufficient to account satisfactorily for the primary isotope effect and whether variation in the  $B$  factor can account satisfactorily for the secondary isotope effect; they can also provide some insight into the nature of the process responsible for two particle loss (i. e., 2H from C<sub>12</sub>H<sub>10</sub>).

The ratio,  $k_{\text{H}}/k_{\text{D}}$  for rupture of C-H in C<sub>12</sub>H<sub>10</sub><sup>+</sup> relative to rupture of C-D in C<sub>12</sub>D<sub>10</sub><sup>+</sup> thus calculated is

$$k_{\text{H}}/k_{\text{D}} = 1.77 \nu_{\text{H}}/\nu_{\text{D}}, \quad (12)$$

and for rupture of C-T bonds, the anticipated value is

$$k_{\text{H}}/k_{\text{T}} = 2.11 \nu_{\text{H}}/\nu_{\text{T}}, \quad (13)$$

where  $\nu_{\text{H}}$ ,  $\nu_{\text{D}}$  and  $\nu_{\text{T}}$  are the frequency factors of the quasi-equilibrium theory. If we allow these frequency factors to vary according to the reduced mass expression, then  $k_{\text{H}}/k_{\text{D}} = 2.46$  and the anticipated value of  $k_{\text{H}}/k_{\text{T}} = 3.65$ .

The actual value of the primary isotope effect in biphenyl is 1.6—2.1 [32] with an average value of 1.8. Primary isotope effects found for dissociation of other deuterated molecule ions range from about 1.8—1.9 for dissociation of ionized unsaturated compounds to about 2.5—3 for dissociation of ionized saturated hydrocarbons. The data for sequences of partially deuterated compounds which are necessary for proper evaluation of this isotope effect are quite scanty.

Several observations of a qualitative nature about this primary isotope effect can be made immediately. It is apparent that the variables which are important contributors to the magnitude of the calculated isotope effect are the values of  $\bar{E}$ ,  $e_0$  and  $A$ ; with the reasonable choices of these which have been made here, it is apparent that the variation of the change in zero point energy (the  $A$  factor) can account satisfactorily for the magnitude of the primary isotope effect and for the fact that this effect is greater than the reduced mass factor. Because of the greater uncertainty in this sort of calculation, to the choice of variables and to the neglect of specific changes in the frequency factor between biphenyl and biphenyl-d<sub>10</sub> (or between other sets of protonated and deuterated molecules), we hesitate to attach more than empirical interest to the calculated ratio. However, we see no reason why predicted magnitude of the tritium isotope effect should not be empirically close to the probable value.

Similar calculations can be made for dissociation of a C-H bond in biphenyl



molecule ions containing various amounts of deuterium, by the use of equation (11) with  $A = 0$ .

The values of  $k_H^H/k_H^{nD}$  thus obtained range from 1.015 for biphenyl- $d_2$  to 1.062 for biphenyl- $d_8$ ; these are much lower than the actual values recorded in Table II. The values of  $nB$  are too small by a factor of about 6 to account for the observed secondary isotope effect, at least in the mathematical form employed here for the study of this variable. We conclude that there must be a substantial change in the frequency factor contributing to this secondary isotope effect. When the explicit form of this frequency factor for biphenyl is examined (equation 14) [28]

$$\nu = \sigma(2\pi)^{3q} \frac{(N - \frac{1}{2}L) \pi \frac{I_1^{*1/2}}{n_1^{*1/2}} \pi \nu_k}{(N - \frac{1}{2}L^*) \frac{I_1^{1/2}}{n_1} \pi \nu_1}, \quad (14)$$

where  $\sigma$  is a symmetry number,  $L$  = number of internal rotational degrees of freedom,  $N$  = total number of internal degrees of freedom and  $I$  = reduced moments of inertia (the other symbols have the same meaning as the original reference [28]), it is apparent that any variation in this factor for the several deuterated biphenyls must come as an additional contribution (over and above the non-fixed energy contribution) from the particular vibrational function because biphenyl does not have a real rotational degree of freedom (the single apparent rotation — about the bond between the two rings — is so constrained that it is actually a torsion [37]).

If a similar rate expression (14) is written for the simultaneous breaking of two bonds (two-particle loss from biphenyl molecule-ions) [32] with a frequency factor which must be about  $10^{-3}$  of that for single-bond breaking [35], an  $E' = 9.5$  and a computed value of  $e_0 = 2.0$ , then a rough value for  $k_{2H}/k_{2D}$  is found to be as in (15),

$$k_{2H}/k_{2D} = 2.48 \nu_{2H}/\nu_{2D} \quad (15)$$

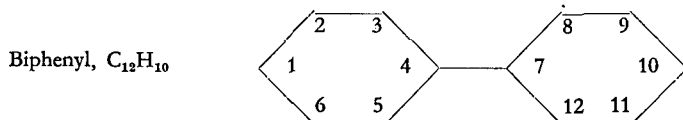
and it is apparent that the energy term is about the same for double-particle loss. It can be seen from Table II that the experimental isotope effect for double-particle hydrogen and deuterium loss from biphenyl molecule-ions is about the same as single-particle loss. We hesitate to draw any sweeping conclusions from this approximation but feel that it indicates a worthwhile line of endeavour for future investigation.

There are a few miscellaneous comments about the foregoing application of the quasi-equilibrium theory. The recent very precise measurement of STEINER *et al.* [29] using photoionization data for a great many of the lower alkanes has tended to destroy much confidence in the quantitative application of the quasi-equilibrium theory. It has also been observed that even the reasonably successful empirical applications of the theory attain success only when the effective number of molecular degrees of freedom are taken as some fraction [30] (ranging from 0 to 1.20 of the total number of degrees of freedom, with no apparent systematic variation from molecule to molecule or from process to process within the same molecule [29]). The calculations which we have made give ratios of reasonable orders of magnitude only when nearly the full number of degrees of freedom is used, and successful calculation for the secondary isotope effect would require a large multiple of the actual number of degrees of freedom if this effect were to be attributed only to change in the non-fixed energy.

The necessity for the employment of the full number of degrees of freedom for

successful calculation of primary isotope effects is a further indication that a substantial contribution to these isotope effects must be looked for in the effect of deuterium substitution upon the frequency factor. We say this because the energy levels in an aromatic molecule possess spacing very far from the close spacing which ROSENSTOCK *et al.* take as a requisite for the necessary rapid equilibration of energy in the quasi-equilibrium theory. The wide spacing of actual energy levels has been mentioned for other molecules [29] but is particularly acute for aromatic molecules because of the existence of a separate, low-energy band of widely spaced energy levels for *pi* electrons (see Table III), together with the probability that the

TABLE III  
ENERGY LEVELS, ELECTRON DENSITIES AND BOND ORDERS



Energy levels:  $\pm 2.2784\beta$ ;  $\pm 1.8912\beta$ ;  $\pm 1.3174\beta$ ;  $\pm 1.0000\beta$ ;  $\pm 0.7046\beta$ . Calculated excitation energy:  $1.4092\beta \cdot 2.39 = 3.37$  eV. Calculated ionization potential:  $0.705\beta \cdot 2.39 + 7.18 = 8.87$ .

Bond	Atom	Ground state	Excited state	Ion
1-2, 1-6, 9-10, 10-11	—	0.6601	0.5485	0.6043
2-3, 5-6, 8-9, 11-12	—	.6766	.7605	.7186
3-4, 4-5, 7-8, 7-12	—	.6188	.4087	.5137
4-7	—	.3697	.6161	.4929
—	1, 10	1.0000	1.0000	.8415
—	2, 6, 9, 11	1.0000	1.0000	.9803
—	3, 5, 8, 12	1.0000	1.0000	.9105
—	4, 7	1.0000	1.0000	.8768

electron removed in ionization of aromatic molecules is most probably one of these isolated *pi* electrons. The rapid internal equilibration of energy is thus most difficult for aromatic molecules, and we would expect that particularly in these cases the effective number of degrees of freedom would be a small fraction of the actual number.

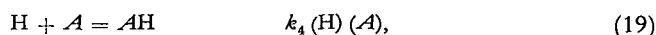
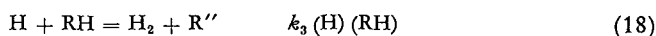
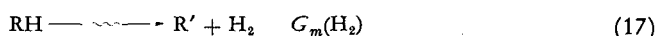
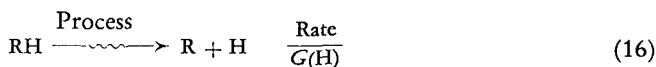
#### D. Isotope effects in molecular dissociation process

Hydrogen formed in the radiolysis (or photolysis) of organic molecules must arise from some combination of three processes: (1) formation and subsequent reaction of hydrogen atoms; (2) formation of molecular hydrogen by unimolecular processes; and (3) formation of hydrogen by bimolecular processes not involving hydrogen atoms [38]. We have just discussed briefly isotope effects in the first sort of process. We would now like briefly to summarize some evidence for the magnitude of deuterium and tritium isotope effects in the second sort of process.

The only process of this sort which has been studied with tritium is the radiolysis of acetic acids labelled with tritium in the methyl group [13]; the methane formed (possible by a molecular dissociation) had nearly the same specific activity as the acetic acid. This displays simply, and not surprisingly, the absence of any secondary isotope effect for elements of a reacting molecule tracer labelled with tritium.

There is evidence of two sorts for the magnitude of isotope effects in molecules labelled with deuterium. The only example of the first sort has been accomplished in this laboratory: the combination of scavenger technique with deuterium labelling.

It has been shown [39] that the effect of dissolved aromatic hydrocarbons upon the hydrogen yield from aliphatic carbinols can be explained quantitatively on the basis of hydrogen-atom scavenging (equations 16—19)



where (17) is the sort of molecular process we are talking about and  $A$  is the concentration of dissolved aromatic hydrocarbon. Data obtained in this way can be fitted into a conventional quenching-type kinetic according to equation (20),

$$\frac{1}{G^0(\text{H}_2) - 1/m[G(\text{H}_2)]} = \frac{1}{G(\text{H})} \left[ 1 - \frac{k_3 \text{RH}}{k_4 A} \right]. \quad (20)$$

This data can then be used in the calculation of the relative values of  $G_m(\text{H}_2)$  and  $G(\text{H})$  for various saturated materials (see Tables IV and V which are reproduced

TABLE IV

#### MECHANISMS OF HYDROGEN FORMATION IN THE RADIOLYSIS OF SATURATED SUBSTANCES

Substance	Solutes used	$G^0(\text{H}_2)$	$G(\text{H})$	$G_m(\text{H}_2)$
Cyclohexane	Benzene, biphenyl benzophenone	5.17	4.10	1.07
Propanol-2	Biphenyl, benzophenone	3.0	1.85	1.15
Methanol	Benzene	5.32	4.20	1.12

TABLE V

#### RELATIVE SCAVENGING EFFICIENCY OF SOLUTES

Solute	Hydrogen atom donor	$k_4/k_4$	Relative Value of $k_4$ Relative Scavenging Efficiency
Benzene	Methanol	72	1.0
	cyclohexane	18	
Biphenyl	Propanol-2	87	6.5
	cyclohexane	116	
Benzophenone	Propanol-2	101	7.5

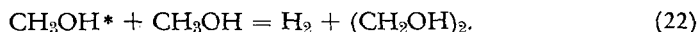
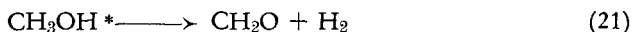
from reference [39]) and in the calculation of the scavenging efficiencies of various aromatic hydrocarbons (Table V). The pertinent fact is that we can deduce from this sort of treatment precisely how much of a scavenger must be used for scavenging

TABLE VI  
RADIOLYSIS OF CH<sub>3</sub>OH AND CH<sub>3</sub>OD SOLUTIONS OF BENZENE

Substrate	Benzene conc. (Mole %)	I/M G (hydrogen)	H <sub>2</sub> (%)	HD (%)	D <sub>2</sub> (%)	G (CH <sub>4</sub> )	G (H)
CH <sub>3</sub> OH	0	5.32	100			0.37	
	4.80	2.00	100			0.169	
	10.0	1.59	100			0.145	4.20
CH <sub>3</sub> OD	0	3.60	40.0	60.0	0	0.62	
	10.58	1.52	46.0	50.0	3	0.27	2.34*

\* Assuming that  $k_4/k_3 = 72$  for this solution as well as for solutions of benzene in methanol.

of a given fraction of the hydrogen atoms generated by the radiation absorption. Thus, if we look at the relative hydrogen formation from CH<sub>3</sub>OD and CH<sub>3</sub>OH and at the effect of 10 mole % dissolved benzene upon these yields, we can make the following statements: (1) replacement of deuterium for hydrogen appears to lower the hydrogen yield; (2) solute benzene also reduces the hydrogen yield, and the yields of hydrogen from both CH<sub>3</sub>OD and CH<sub>3</sub>OH containing 10 mole % benzene are the same; (3) 10 mole % benzene is sufficient, from equation (20) and Table V, to scavenge over 84% of the hydrogen atoms; and, therefore, the yields of hydrogen from the solutions of 10 mole % benzene in methanol represent the yield of hydrogen from the molecular process under discussion. It is then apparent that there is no isotope effect in the formation of this non-radical hydrogen, which from the HD content, is probably formed via at least two processes which can be presented as (21) and (22) [40].



Thus, there does not appear to be any isotope effect in those two types of processes although it must be admitted that a similar study for CD<sub>3</sub>OD and CH<sub>3</sub>OH would be more revealing and precise.

Other studies have indicated that there is a small deuterium isotope effect in such molecular processes. Vacuum ultraviolet photolysis of ethane produces hydrogen [41] entirely by a molecular detachment, since only H<sub>2</sub> and D<sub>2</sub> was produced from a mixture of ethane and ethane-d<sub>6</sub>, and the ratio of H<sub>2</sub>/D<sub>4</sub> formation, in the run of lowest per cent decomposition, was 1.5. A similar effect of the same magnitude has been reported for the radiolysis of ethane and ethane-d<sub>6</sub> mixture [3] by DOREMAN and SAUER [42]. OKABE and MCNESBY [41] report a secondary isotope effect of even greater magnitude, since the formation of methane from the ethane mixture was also by an entirely molecular process and the ratio of CH<sub>4</sub> to CD<sub>4</sub> was about 0.2. This isotope effect is called a secondary isotope effect since the C-C and (perhaps) C-H band are involved in the (possibly) four-centre transition state.

Finally, if the present interpretation of the mechanisms of hydrogen formation from aromatic hydrocarbons are correct [32], then the isotope effect in this process represents the isotope effect in a non-radical bimolecular processes, like (22), and are thus substantial, amounting to  $k_H/k_D$  values which are close to 3.0 for both benzene and biphenyl. They are thus about the largest of the several different types of isotope effects which must be included in any consideration of the use of hydrogen isotopes in radiation chemistry of organic materials.

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## DISCUSSION XI

**N. Getoff** (Austria): Has Mr. Burr any experimental evidence about the exchange between hydrogen, deuterium, and tritium in aqueous solutions of organic compounds, e. g. for various periods of time after the completion of irradiation?

**J. G. Burr** (United States of America): Speaking in very general terms, molecular  $H_2$ , HD,  $D_2$ , HT,  $T_2$  and DT do not exchange with themselves or with organic molecules unless the molecular species (hydrogen or organic) can in some way be efficiently converted to ions, radicals or atoms. Ordinarily there is no exchange between the gaseous hydrogen formed and the liquid unless you use a large amount of tritium and carry out Wilzbach labelling, and then the amount of exchange is very small.

# STUDIES ON THE MECHANISM OF THE CANNIZZARO REACTION

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UNITED STATES OF AMERICA

## Abstract — Résumé — Аннотация — Resumen

**Studies on the mechanism of the Cannizzaro reaction.** An intensive investigation of the mechanism of the Cannizzaro reaction was undertaken. An isotope dilution technique was employed with  $p$ - $t$ - $C_6H_5CHO$  in 74% methanol solution at 100°C in order to determine the presence of a reaction intermediate. The kinetics of the homogeneous benzaldehyde Cannizzaro reaction were measured in 74% methanol at 100°C. The second-order rate constant for the hydrolysis of benzyl benzoate in 74% methanol at 100°C was determined. The kinetics of the hydrolysis of  $p$ - $t$ -benzyl benzoate- $p$ - $t$  were studied in 74% methanol at 100°C. It was shown that an intermediate ester is not present in the early stages of the Cannizzaro reaction. It was demonstrated that the hydrolysis of benzyl benzoate under Cannizzaro conditions is very fast. Calculation of the concentrations of ester which should be present in the Cannizzaro reaction showed that these quantities are well within the range of detection of the sensitive radiotracer technique employed. It was concluded that the mechanism of the Cannizzaro reaction involves an intermolecular hydride ion shift rather than an intramolecular H: transfer. A deuterium isotope effect of 0.50 found for this reaction indicates that the proton transfer takes place in a rapid subsequent step rather than simultaneously with the hydride shift.

**Etude de mécanisme de la réaction de Cannizzaro.** Les auteurs ont procédé à une étude approfondie du mécanisme de la réaction de Cannizzaro. Toutes les expériences qu'ils décrivent ont été réalisées dans une solution de méthanol à 74%, à 100°C. Dans ces conditions, ils ont appliqué une technique de dilution isotopique au  $p$ - $T$ - $C_6H_5CHO$  afin de déceler la présence d'un produit de réaction intermédiaire, et ils ont mesuré la cinétique de la réaction homogène de Cannizzaro avec le benzaldéhyde. Ils ont déterminé la constante de vitesse de réaction de deuxième ordre pour l'hydrolyse du benzoate de benzyle dans le même milieu et étudié la cinétique de l'hydrolyse du  $p$ - $T$ -benzoate de benzyle- $p$ - $T$ . Ils ont montré qu'aucun ester intermédiaire n'apparaît au cours des étapes initiales de la réaction de Cannizzaro. Il a été prouvé que, dans les conditions habituelles de cette réaction, l'hydrolyse du benzoate de benzyle est très rapide. Le calcul des concentrations d'ester qui devraient être atteintes durant la réaction de Cannizzaro montre que ces concentrations sont d'un ordre de grandeur qui permet de les détecter au moyen d'indicateurs radioactifs grâce à la sensibilité de la méthode employée. Les auteurs ont conclu que le mécanisme de la réaction de Cannizzaro implique un déplacement intermoléculaire des ions hydrure plutôt qu'un transfert de H: intramoléculaire. La constatation d'un effet isotopique de 0,50 dû au deutérium au cours de cette réaction indique que le transfert de proton a lieu dans une phase subséquente rapide et ne coïncide pas avec le déplacement de l'ion hydrure.

**Исследование механизма реакции Канниццаро.** Предпринималось интенсивное исследование механизма реакции Канниццаро. Для определения наличия промежуточной реакции применялся метод изотопного раствора  $p$ - $t$ - $C_6H_5CHO$  в 74%-ном метаноловом растворе при температуре 100°C. Кинетика гомогенного бензойного альдегида реакции Канниццаро измерялась в 74%-ном метаноле при температуре 100°C. Определялась постоянная скорости второго порядка для гидролиза бензил бензоата в 74%-ном метаноле при температуре 100°C. Исследовалась кинетика гидролиза  $p$ - $t$ -бензил бензоат- $p$ - $t$  в 74%-ном метаноле при температуре 100°C. Было показано, что на ранних стадиях реакции Кан-

нищцаро промежуточный сложный эфир отсутствует. Было продемонстрировано, что гидролиз бензил бензоата в условиях реакции Канниццаро является очень быстрым. Вычисление концентраций сложного эфира, который должен присутствовать в реакции Канниццаро, показало, что эти количества находятся в диапазоне определения используемого чувствительного метода радиоиндикации. В результате было дано заключение, что механизм реакции Канниццаро влечет за собой в первую очередь межмолекулярное гидридное смещение ионов, а не внутримолекулярное H перемещение. Обнаруженный для этой реакции эффект изотопа дейтерия в 0,50 указывает на то, что смещение протона происходит с быстрой последовательностью, а не одновременно со смещением гидрида.

**Estudio del mecanismo de la reacción de Cannizzaro.** Los autores han investigado a fondo el mecanismo de la reacción de Cannizzaro. Todos los experimentos descritos fueron realizados con una solución metanólica al 74% y a 100°C de temperatura. Por una técnica de dilución isotópica, estudiaron la posible formación de un producto intermedio a partir del  $p\text{-T-C}_6\text{H}_4\text{CHO}$ ; también midieron la cinética de la reacción de Cannizzaro homogénea para el benzaldehído. Determinaron la constante de velocidad de segundo orden de la hidrólisis del benzoato de bencilo y estudiaron la cinética de la hidrólisis del  $p\text{-T-benzoato de } p\text{-T-bencilo}$ . Demostraron que no se forma ester intermedio en las fases iniciales de la reacción y que la hidrólisis del benzoato de bencilo tiene lugar muy rápidamente en las condiciones en que se produce la reacción de Cannizzaro. El cálculo de la concentración de ester que debería alcanzarse en dicha reacción demuestra que esa cantidad tendría que poder detectarse con facilidad en razón de la alta sensibilidad de la técnica de radio-trazadores empleada. Los autores llegan a la conclusión de que en la reacción de Cannizzaro se produce un desplazamiento intermolecular de ión hidruro y no una transferencia intramolecular de hidrógeno. El efecto isotópico de 0.50 debido al deuterio que encontraron en esta reacción indica que la transferencia de protón tiene lugar en una etapa subsiguiente y rápida, y que no coincide con el desplazamiento del ión hidruro.

## A. Introduction

The CANNIZZARO reaction [1—4] has been subjected to a variety of careful kinetic and mechanistic investigations. It is characteristic of aldehydes which have no hydrogen on the alpha carbon atom, such as formaldehyde, pivaldehyde, aromatic aldehydes and a number of heterocyclic aldehydes. Kinetic analyses made by numerous investigators have shown that the Cannizzaro reaction of aromatic aldehydes in hydroxylic solvents, notably aqueous methanol, pure methanol and aqueous dioxane, is first order in  $\text{OH}^-$ , second order in  $\phi\text{CHO}$  and third order over-all [5—9].

A free radical mechanism for the Cannizzaro reaction was proposed by WEISS [10]. His suggestion was based largely on observations by KHARASCH and FOY [11] and by URUSHIBARA and TAKEBAYASHI [12] that the heterogeneous Cannizzaro reaction is catalyzed by peroxides. Subsequently KHARASCH and SNYDER [13] demonstrated that the heterogeneous reaction is polar but that the mechanism is different in the two liquid phases. However, ALEXANDER [8] and GEIB [14] provided evidence that the Cannizzaro reaction is completely unaffected by the presence of free radical initiators or inhibitors, indicating that the homogeneous reaction proceeds by an ionic rather than a free radical mechanism.

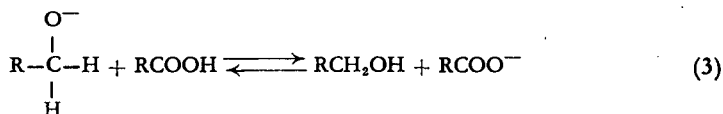
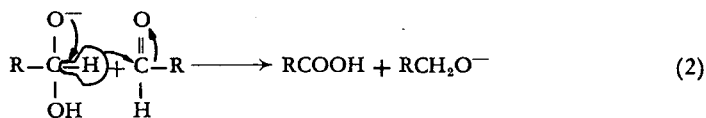
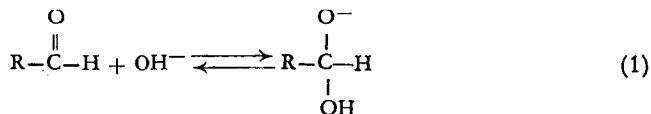
FREDENHAGEN and BONHOEFFER [15] demonstrated that hydrogen transfer from one aldehyde group to another takes place directly without exchange with the medium by showing that no carbon-bound deuterium appears in the products when the reaction is carried out in heavy water.



## B. Mechanisms

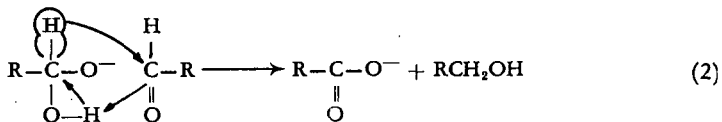
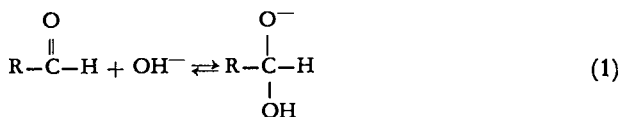
Four mechanism are possible for the homogeneous Cannizzaro reaction:

### (a) THE INTERMOLECULAR (HAMMETT) MECHANISM



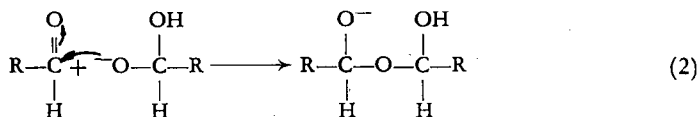
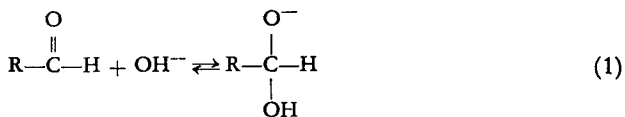
This mechanism [16] involves formation of an aldehydoxide ion by addition of  $\text{OH}^-$  to aldehyde (1), an intermolecular hydride shift to give an acid and an alkoxide ion (2) and a final rapid proton transfer (3)

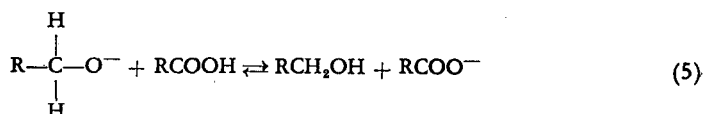
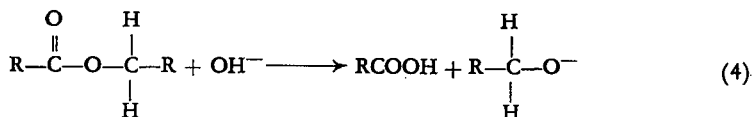
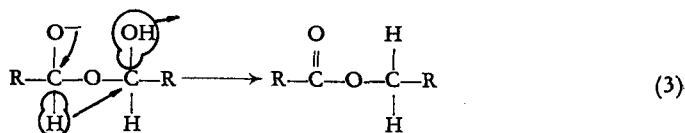
### (b) CYCLIC, CONCERTED INTERMOLECULAR MECHANISM



In this mechanism, the first step is also the formation of an aldehydoxide ion. The second step involves a cyclic, concerted shift of a hydride and a proton from the aldehydoxide ion to a neutral aldehyde in the slow step to form the products directly.

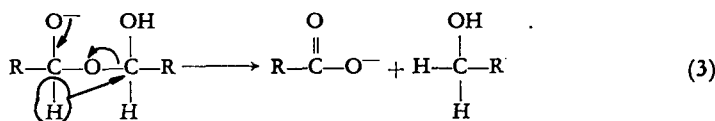
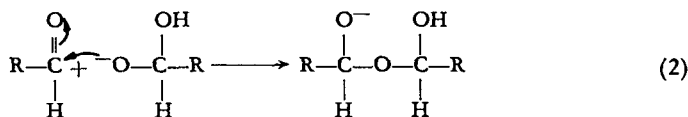
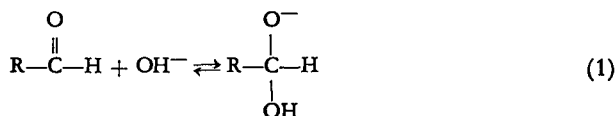
### (c) INTRAMOLECULAR (GEISSMAN) MECHANISM





In this mechanism [2], steps 1 and 5 are the same as in (a) above. The second step involves the attack of an aldehydoxide ion on a neutral aldehyde followed by an intramolecular hydride shift (3) to produce an ester intermediate which is rapidly saponified (4). Either step 2 or 3 could be rate controlling.

(d) MODIFIED INTRAMOLECULAR MECHANISM



The first two steps of this mechanism are the same as in (c). In the third step, there is a 1.3 hydride shift which breaks the ether linkage instead of expelling the hydroxyl group. Either step 2 or step 3 could be rate-determining.

### C. Results and Discussion

If the intramolecular (Geissman) mechanism is correct, it should be possible to detect the presence of an intermediate ester. Since the steady state concentration of benzyl benzoate, if it is formed in the benzaldehyde Cannizzaro reaction, will be low (because of the high concentration of sodium hydroxide, 0.25 M, and the high temperature, 100 °C), a sensitive radiochemical method will be needed for its measurement. Accordingly, it was decided to synthesize benzaldehyde-p-t and to use it in an investigation of the kinetics of the homogeneous Cannizzaro reaction at 100 °.

Benzaldehyde-p-t was prepared from toluene-p-t by side-chain photo-chlorination, followed by alkaline hydrolysis, steam distillation, conversion of the aldehyde to

the sodium bisulfite adduct and purification by distillation under reduced pressure in an inert gas atmosphere [17]. The toluene-p-t had been previously made by a Grignard reaction with p-bromotoluene in which tritium chloride, prepared from a heated mixture of tritium and protium oxides and benzoyl chloride, was swept into the reaction mixture by a stream of dry nitrogen [18].

The kinetics of the homogeneous benzaldehyde Cannizzaro reaction at 100°C were studied by means of a modification of the method of MOLT [5] and ALEXANDER [8]. The values obtained for the third-order rate constant are in good agreement with the results of earlier investigations, as shown in Table I.

TABLE I  
THIRD-ORDER RATE CONSTANTS FOR CANNIZZARO REACTION AT 100°  
(2 C<sub>6</sub>H<sub>5</sub>CHO + NaOH → C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH + C<sub>6</sub>H<sub>5</sub>COONa)

Investigator	Medium	Third-order rate constant X 10 <sup>4</sup> (l <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup> )
Molt	50% methanol	2.28 ± 0.08
Molt	50% methanol	2.38 ± 0.10
Wiberg	67% methanol	2.22 ± 0.10
This work (benzaldehyde)	74% methanol	2.36 ± 0.16*
This work (benzaldehyde-p-t)	74% methanol	2.45 ± 0.33*

\* The values reported have not been corrected for the small reaction of base with glass discovered later.

The isotope dilution technique [19] was employed in determination of the quantity of radioactive benzyl benzoate which might have been formed as a reaction intermediate. Large, known amounts of unlabelled benzyl benzoate were added to the samples from the kinetic measurements. Separation of the benzyl benzoate

TABLE II  
DETERMINATION OF p-t-BENZYL BENZOATE-p-t IN THE  
BENZALDEHYDE-p-t CANNIZZARO REACTION AT 100°

Time (sec)	No. of crystallizations	M. P. of benzyl benzoate	Counts/mm*
1796	1	15.5—16.0	90,500
1960	1	—	88,100
7320	1	—	252,000**
14280	1	—	189,000
7320	2	—	162,000
1789	3	18.5—18.6	167***
1796	3	17.9—18.7	154
4740	3	17.0—17.5	150
8700	3	18.4—18.9	145
15240	3	17.6—18.5	238
3840	4	18.5—19.4	173†

Specific activity of benzaldehyde-p-t = 157 μc/mM. Background, results of 3 separate measurements = 110, 151, 186 cpm.

\* Computed on basis of total amount of benzyl benzoate added in each case.

\*\* Scavengers added: 0.2 ml OCHO, 0.1 ml OCH<sub>2</sub>OH, 0.1 g OCOOH.

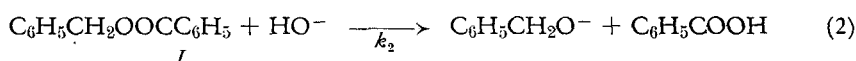
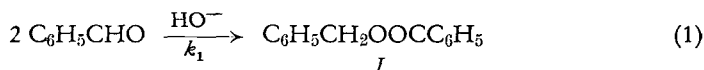
\*\*\* Scavengers added: 0.5 ml OCHO, 0.5 ml OCH<sub>2</sub>OH, 0.5 g OCOOH.

† Scavengers added: 0.2 ml OCHO, 0.1 ml OCH<sub>2</sub>OH, 0.1 g OCOOH.

was achieved by fractional crystallization from the reaction solutions cooled to 0°C in an ice-water bath. Liquid scintillation counting was utilized for measurement of the activity of the benzyl benzoate recovered.

No benzyl benzoate was detected in any of the reaction mixtures from the benzaldehyde-p-t Cannizzaro reaction at 100°C when care was taken to assure that the recovered benzyl benzoate was pure as verified by melting-point determinations. The results in Table II show that, of sufficient crystallizations were performed, radioactive impurities were eliminated and scavengers were found not to be necessary.

These results indicate that either no intermediate is formed in the Cannizzaro reaction or that the specific activity of the benzaldehyde-p-t employed was not sufficiently high for detection of a very transitory species. To settle this question, we measured the second-order rate constant for the hydrolysis of benzyl benzoate under Cannizzaro conditions. The value of  $k_2$  in 74% methanol at 100° was found to be 0.054 l mole<sup>-1</sup> sec<sup>-1</sup> and was used in a steady-state approximation for calculation of the concentration of ester which should accumulate in the Cannizzaro reaction at any given time, assuming the intramolecular (Geissman) mechanism. The concentration of intermediate *I* at any given time after the start of the Cannizzaro reaction was computed as follows:



$$\frac{dI}{dt} = k_1 (\text{C}_6\text{H}_5\text{CHO})^2 (\text{HO}^-) - k_2 (I) (\text{HO}^-). \quad (3)$$

Assuming steady state conditions,

$$(I) = \frac{k_1 (\text{C}_6\text{H}_5\text{CHO})^2}{k_2}. \quad (4)$$

The calculated values for the concentration of the intermediate ester vary between 10<sup>-4</sup> to 10<sup>-3</sup> M/l during the early stages of the Cannizzaro reaction, as can be seen by examination of Table III. These concentrations are well within the range

TABLE III  
BENZYL BENZOATE PRESENT IN CANNIZZARO REACTION  
ASSUMING INTRAMOLECULAR (GEISSMAN) MECHANISM

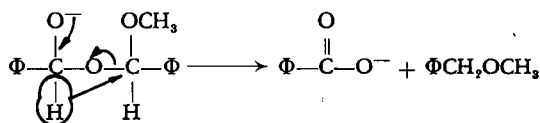
Time (sec)	a-x (mole/l)	(a-x) <sup>2</sup> (mole/l)	(I) (mole/l X 10 <sup>4</sup> )
1789	0.2334	0.05448	9.89
1896	0.2320	0.05382	9.77
3840	0.2122	0.04503	8.18
4740	0.2054	0.04219	7.66
7320	0.1834	0.03364	6.11
8700	0.1762	0.03105	5.63
14280	0.1412	0.01994	3.62
15240	0.1363	0.01858	3.37

Initial concentration of benzaldehyde-p-t = 0.2546 mole/l

(I) = concentration of benzyl benzoate as assumed reaction intermediate.

of detectability of the tritium tracer technique employed, where it was found that  $10^{-7}$  to  $10^{-6}$  M/l of p-t-benzyl benzoate-p-t could be easily measured. These results indicate that the hydride transfer is intermolecular.

However, before a mechanism involving an intramolecular hydride shift could be unequivocally ruled out, it was necessary to show that mechanism (d) is not correct. A shift of the sort depicted in (d) might be expected in hemiacetal hydrolysis and, if it occurred in methanol solution where methoxide ion is a possible attacking species, should result in the accumulation of a significant amount of methyl benzyl ether at the end of the benzaldehyde Cannizzaro reaction.



To settle this point, we used gas chromatography to examine the reaction mixture at the end of a Cannizzaro run. The products were analyzed with a chromatograph equipped with a 6½ ft 20 M Carbowax-chromosorb (80–100 mesh) column. Helium at an inlet pressure of 15.0 psi was the carrier gas. The results showed sharp separation of methanol, benzaldehyde and benzyl alcohol, but methyl benzyl ether was not found. In a separate run in which methyl benzyl ether was added at the beginning of the reaction, it was shown that this ether is not destroyed under Cannizzaro conditions.

Deuterium isotope effect measurements were employed to distinguish between the intermolecular mechanism (a) and the cyclic, concerted intermolecular mechanism (b). Since the cyclic mechanism involves a proton transfer in the slow step, a large isotope effect ( $k_H/k_D$ ) would be expected [20, 21]. The rate constants for the Cannizzaro reaction at 100° of benzaldehyde with sodium deuterioxide in 74% methanol-d and with sodium hydroxide in 74% methanol were determined. The results are summarized in Table IV.

TABLE IV

SUMMARY OF THIRD-ORDER RATE CONSTANTS FOR THE BENZALDEHYDE CANNIZZARO REACTION WITH SODIUM DEUTEROXIDE IN 74% METHANOL-d AND SODIUM HYDROXIDE IN 74% METHANOL AT 99.5°

Run	Initial Conc. Benzaldehyde (M)	Initial Conc. Base (M)	$k^3$ (l <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup> )
1	0.5508	0.2754 OD <sup>-</sup>	$3.62 \times 10^{-4} \pm 0.12$
2	0.5272	0.2636 OH <sup>-</sup>	$1.79 \times 10^{-4} \pm 0.10$
3	0.5352	0.2676 OH <sup>-</sup>	$1.86 \times 10^{-4} \pm 0.11$
4	0.5744	0.2872 OD <sup>-</sup>	$3.33 \times 10^{-4} \pm 0.13$

Sodium deuterioxide in methanol-d was found to react about 90% faster than sodium hydroxide in methanol in the benzaldehyde Cannizzaro reaction ( $k_H/k_D = 0.52$ ). This result eliminates the cyclic, concerted intermolecular mechanism (b) since the proton must be transferred after the rate-determining step\*. The fact

\* J. HINE and H. W. HAWORTH [*J. Amer. chem. Soc.* **80** (1958) 2274] found the rearrangement of benzyl to be about 85% faster in D<sub>2</sub>O-dioxane than if was in H<sub>2</sub>O-dioxane and concluded that the phenyl migration precedes the proton transfer in this reaction.

that  $\text{OD}^-$  in methanol-d reacts faster than does  $\text{OH}^-$  in methanol is attributed to the greater basicity and nucleophilicity of the deuteroxide ion [22].

#### D. Conclusion

It is concluded from the results of this investigation that the mechanism of the homogeneous Cannizzaro reaction involves an intermolecular hydride transfer in the rate-determining step followed by a rapid proton transfer.

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# CORRELATION OF TRITIUM AND DEUTERIUM ISOTOPE EFFECTS\*

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Abstract — Résumé — Аннотация — Resumen

**Correlation of tritium and deuterium isotope effects.** The theory of relative tritium-protium and deuterium-protium isotope effects is developed for both rate and equilibrium processes. It is shown that the relative effects in equilibrium processes vary with the strength of the chemical bonding and the temperature. A lower limit of 1.33 and an upper limit of 1.55 is established for  $\ln a_{T-H}/\ln a_{D-H}$ . Detailed calculations are given for a number of simple molecules.

It is shown that the temperature independent frequency factor in rate processes increases the ratio  $\ln(k_H/k_T)/\ln(k_H/k_D)$  above the values found in equilibrium processes. Equations are given from which the increment can be calculated. It is shown that relative tritium-protium versus deuterium-protium isotope effects may be of diagnostic use in characterizing secondary isotope effects and tunnelling in chemical reactions.

Detailed calculations are given for three types of processes involving water: (1) equilibration with hydrogen, (2) distillation, and (3) electrolysis. In these three different processes  $a_{D-H}$  varies from  $5 \times 10^{-2}$  to 10, yet in  $(a_{T-H})/\ln(a_{D-H})$  is calculated to be in the range 1.33–1.40 for all three processes, in excellent agreement with experiment.

**Corrélation entre les effets isotopiques du tritium et du deutérium.** L'auteur développe la théorie des effets isotopiques relatifs tritium-protium et deutérium-protium pour les réactions d'équilibre et les processus cinétiques. Il montre que dans les réactions d'équilibre les effets relatifs varient en fonction de la résistance des liaisons chimiques et de la température. Les limites inférieure et supérieure sont respectivement 1,33 et 1,55 pour le rapport  $\ln a_{T-H}/\ln a_{D-H}$ . Des calculs détaillés sont présentés pour un certain nombre de molécules simples.

L'auteur montre que, dans les processus cinétiques, le facteur de fréquence indépendant de la température porte le rapport  $\ln(k_H/k_T)/\ln(k_H/k_D)$  au-delà des valeurs constatées pour les réactions d'équilibre. Il donne des équations permettant de calculer l'augmentation. Il montre, d'autre part, que les effets isotopiques relatifs tritium-protium et deutérium-protium peuvent être utilisés à des fins d'analyse, pour caractériser les effets isotopiques secondaires dans les réactions chimiques.

L'auteur présente des calculs détaillés pour trois types de processus dans lesquels l'eau intervient: 1° équilibrage avec l'hydrogène, 2° distillation et 3° électrolyse. Dans ces trois processus,  $a_{D-H}$  varie de  $5 \cdot 10^{-2}$  à 10, mais le rapport  $\ln(a_{T-H})/\ln(a_{D-H})$  reste compris entre 1,33 et 1,40, ce qui concorde parfaitement avec l'expérience.

**Корреляция изотопических эффектов трития и дейтерия.** В докладе дается развитие теории относительных изотопических эффектов трития-протия и дейтерия-протия в применении как к кинетическому процессу, так и к процессу равновесия. Показано, что относительные эффекты в процессах равновесия варьируются по мере увеличения химической связи и температуры. Установлен нижний предел в 1.33 и верхний предел в 1.55 для  $\ln a_{T-H}/\ln a_{D-H}$ . Даются подробные расчеты для целого ряда простых молекул.

В докладе показано, что независимый от температуры коэффициент частоты в кинетических процессах увеличивает соотношение  $\ln(k_H/k_T)/\ln(k_H/k_D)$  по сравнению с величинами, наблюдаемыми в процессах равновесия. Приводятся уравнения, по которым можно вычислить прирост. Показано, что относительные изотопические эффекты трития-протия и дейтерия-протия могут быть исполь-

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зованы в диагностике для характеристики вторичных изотопических эффектов и туннельных эффектов в химических реакциях.

В докладе даны подробные расчеты для трех видов процессов, связанных с водой: 1) уравнивание с водородом, 2) дистиллирование и 3) электролиз. В этих трех различных процессах  $\alpha_{T-H}$  изменяется в пределах от  $5 \times 10^{-2}$  до 10, однако для  $\ln(\alpha_{T-H})/\ln(\alpha_{D-H})$  вычислен предел 1.33—1.40 для всех трех процессов, что точно совпадает с данными эксперимента.

**Correlación entre los efectos isotópicos del tritio y del deuterio.** La memoria expone la teoría de los efectos isotópicos relativos tritio-protio y deuterio-protio en los procesos cinéticos y en los procesos en equilibrio. Demuestra que los efectos relativos en los procesos en equilibrio varían con la fuerza del enlace químico y la temperatura. Establece un límite inferior de 1,33 y un límite superior de 1,55 para el cociente  $\ln \alpha_{T-H}/\ln \alpha_{D-H}$  y efectúa los cálculos detallados correspondientes a varias moléculas simples.

La memoria demuestra que en virtud del factor de frecuencia independiente de la temperatura que corresponde a los procesos cinéticos, la razón  $\ln(k_H/k_T)/\ln(k_H/k_D)$  aumenta por encima de los valores encontrados para los procesos en equilibrio, e indica ecuaciones que permiten calcular el incremento. Demuestra asimismo que los cocientes de los efectos isotópicos relativos del tritio-protio y del deuterio-protio pueden servir para caracterizar los efectos isotópicos secundarios y de túnel en las reacciones químicas.

El autor efectúa cálculos detallados para tres tipos de procesos en los que interviene el agua: 1) puesta en equilibrio con hidrógeno, 2) destilación y 3) electrólisis. En estos tres procesos,  $\alpha_{D-H}$  varía entre  $5 \cdot 10^{-2}$  y 10, pero se calcula que el valor de  $\ln(\alpha_{T-H})/\ln(\alpha_{D-H})$  oscila entre 1,33 y 1,40 para los tres procesos, lo que concuerda satisfactoriamente con los resultados experimentales.

## Introduction

Hydrogen isotope effects encompass the range from a few per cent to an order of magnitude per hydrogen atom substituted in both rate and equilibrium processes at room temperature. The small effects occur in systems where there is no significant change in the chemical bonding of the labelled hydrogen atom in the net reaction. Examples of such effects are liquid-vapour equilibria, solvent isotope effects in the absence of acid-base equilibria, secondary isotope effects and isotopic disproportionation equilibria, e. g.  $2\text{HDO} = \text{H}_2\text{O} + \text{D}_2\text{O}$ . It has been shown [1] that the largest effects in isotopic disproportionation equilibria arise in the reaction



$$K = (4) (0.64) \text{ at } 298^\circ\text{K} [2].$$

Yet, even in this disproportionation, the fractionation factor is  $(0.64)^{1/2}$  or 0.80 per tritium atom. In all of the processes mentioned, the chemical or valence bonding of the labelled hydrogen remains essentially unaltered in the reaction. These small isotope effects can be multiplied by multiple substitution, and the over-all rate constant for the solvolysis of *t*-amyl chloride- $\text{d}_3$  is smaller than the unsubstituted compound by a factor of 2.35 at  $25^\circ\text{C}$  [3]. Large kinetic and equilibrium isotope effects arise when the labelled hydrogen undergoes a reaction where it is strongly bonded in the reactant and loosely bound (free atom) in the product or transition state [4, 5]. A fractionation factor of 6.75 is obtained in the distribution of tritium between water vapour and hydrogen gas [6] and 14 in the electrolysis of tritiated water [7].

The present investigation was undertaken to determine whether or not any correlations can be made between tritium and deuterium isotope effects. Particular



attention has been given to the fact that these isotope effects cover several orders of magnitude. If a correlation is possible, then the large body of experimental data and theoretical calculations on deuterium isotope effects would be useful in studies with tritium. In many low-level experiments with tritium, the material is enriched prior to low-level counting, and the measured deuterium enrichment is used in the calibration of the tritium enrichment [8, 9]. The basis of this method is that  $\alpha_{T-H}/\alpha_{D-H}$ , the relative tritium-to-deuterium fractionation factors relative to protium, is a constant. This has been established by KAUFMAN *et al.* [8] for the electrolysis of water but has been questioned recently by SCHUMACHER [9]. If a correlation can be found between tritium and deuterium isotope effects, based on systems without such quantum mechanical effects as tunnelling, then abnormal ratios of tritium to deuterium isotope effects would provide evidence for such phenomena in reactions involving hydrogen and its isotopes.

### Theory of relative effects

A treatment of relative tritium to deuterium isotope effects with respect to protium has been given by SWAIN *et al.* [10]. These authors considered only the zero-point energy contribution and the effect of the Boltzmann excitation. All hydrogen vibrations were assumed to be lowered by  $(2)^{1/2}$  and  $(3)^{1/2}$  by deuterium and tritium substitution respectively. They found  $\ln \alpha_{T-H}/\ln \alpha_{D-H} = 1.44$ ,  $\alpha_{T-H} = K_H/K_T$ ,  $\alpha_{D-H} = K_H/K_D$ . The treatment neglects temperature-independent entropy effects to  $\ln \beta$  and  $\ln \alpha$ . Further, it is clear from the product rule [11] that not all the hydrogen vibrations can be shifted by  $(2)^{1/2}$  or  $(3)^{1/2}$  by deuterium and tritium substitution respectively. In particular, the change in the moments of inertia of the molecule by isotopic substitution will reduce the isotope shifts in bending vibrations.

The equilibrium isotopic fractionation between two chemical species, each of which has just one isotopically replaceable atom, is just the equilibrium constant for the exchange reaction



$$\alpha_{D-H} = K_2 = (DX/HX)/(DY/HY) \quad (4)$$

$$\alpha_{T-H} = K_3 = (TX/HX)/(TY/HY). \quad (5)$$

If there are two or more isotopically equivalent atoms in the molecule, the isotopic fractionation factor is directly related to the reduced partition function ratio [5],  $s/s' f$

$$H_n X + H_{m-1} TY = H_{n-1} TX + H_m Y \quad (6)$$

$$\alpha_{T-H} = \frac{\beta(H_n X)}{\beta(H_m Y)} = \frac{s/s' f_T(H_n X)}{s/s' f_T(H_m Y)} = (m/n) K_6 \quad (7)$$

where

$$\beta(H_n X) = (T/H)_{H_n X} = \frac{1}{n} \frac{(H_{n-1} TX)}{(H_n X)} \quad (8)$$

$$\beta(H_m Y) = (T/H)_{H_m Y} = \frac{1}{m} \frac{(H_{m-1} TY)}{(H_m Y)} \quad (9)$$

Equations 6—9 have been shown to be valid even when there is appreciable isotopic fractionation between  $H_n X$  and  $H_m Y$  [12]. A singular exception is the molecular

species  $H_2$  at low temperature. The relative tritium and deuterium fractionation factors in an equilibrium system are

$$\frac{\ln \alpha_{T-H}}{\ln \alpha_{D-H}} = \frac{\ln s/s' f_{T-H}(X) - \ln s/s' f_{T-H}(Y)}{\ln s/s' f_{D-H}(X) - \ln s/s' f_{D-H}(Y)}. \quad (10)$$

Since the logarithm of the vapour pressure ratio of isotopic molecules can be expressed in terms of  $\ln s/s' f$  (solid, liquid) —  $\ln s/s' f$  (gas) [13], equation 10 is not restricted to gaseous reactions.

We consider first the high temperature approximation to  $\ln s/s' f$  [1]

$$\ln s/s' f = \frac{1}{24} \left( \frac{b}{kT} \right)^2 \left( \frac{1}{m_H} - \frac{1}{m(T,D)} \right) a_{ii} + \dots \left[ \frac{b}{kT} \left( \frac{a_{ii}}{m_H} \right)^{1/2} < 2\pi \right], \quad (11)$$

where  $m_H$ ,  $m_D$ ,  $m_T$  are the masses of protium, deuterium and tritium respectively, and  $a_{ii}$  is the Cartesian force constant for the displacement of this atom in the molecule. From equations 10 and 11 we obtain

$$\frac{\ln \alpha_{T-H}}{\ln \alpha_{D-H}} = 4/3. \quad (12)$$

One can show that 4/3 is a lower limit to  $\frac{\ln \alpha_{T-H}}{\ln \alpha_{D-H}}$  since

$$\frac{\frac{1}{m_H} - \frac{1}{m_T}}{\frac{1}{m_H} - \frac{1}{m_D}} < \frac{\left( \frac{1}{m_H} \right)^{1/2} - \left( \frac{1}{m_T} \right)^{1/2}}{\left( \frac{1}{m_H} \right)^{1/2} - \left( \frac{1}{m_D} \right)^{1/2}}. \quad (13)$$

We now consider low temperature systems, i. e. systems for which the Boltzmann excitation factors,  $(1 - e^{-u})$ , are small. For such systems the result of SWAIN *et al.* [10] is an upper limit to  $\ln s/s' f_{T-H}/\ln s/s' f_{D-H}$ . For all systems there will always be a correction from the Boltzmann excitation in tritium compounds. The term  $\Sigma^{3n-6} \ln u_{iT}/u_{iD}$  is always negative and lowers the zero point energy effect. Finally, the operation of the product rule lowers the relative T to D zero-point energy effects from 1.44. Further, the over-all relative T—D fractionation with respect to protium is not determined by  $\ln s/s' f_{T-H}(X)/\ln s/s' f_{D-H}(X)$ . In Table I we give the values of  $\ln s/s' f_T/\ln s/s' f_D$  for a number of simple molecules.

TABLE I  
RELATIVE TRITIUM AND DEUTERIUM PARTITION FUNCTION RATIOS

Molecule	$\ln s/s' f_D$	$\ln s/s' f_T/\ln s/s' f_D$		
	298° K	298° K	600° K	1000° K
$H_2$	1.215	1.37 [2]	1.36 [2]	1.36 [14]
HF	2.359	1.42 [2,14]	1.40 [2,14]	1.37 [2,14]
HCl	1.669	1.41 [2,14]	1.39 [2,14]	
HBr	1.469	1.41 [2,14]	1.38 [2,14]	
HI	1.245	1.40 [5,14]	1.37 [5,14]	1.34 [5,14]
$H_2O$	2.524	1.38 [2]	1.36 [2]	1.33

We note that they lie in the range 1.33—1.44. Although the range of  $\ln s/s' f_T/\ln s/s' f_D$  is small, a definite trend is obvious and to be expected from the theory. The high values are associated with strong chemical bonds and the large mass of the atom to which the hydrogen is bonded.

The relative T—H/D—H fractionation factors can then be written

$$\frac{\ln \alpha_{T-H}}{\ln \alpha_{D-H}} = \frac{a \ln s/s' f_D(X) - b \ln s/s' f_D(Y)}{\ln s/s' f_D(X) - \ln s/s' f_D(Y)} \quad (14)$$

$$= a + (a-b) \frac{\ln s/s' f_D(Y)}{\ln s/s' f_D(X) - \ln s/s' f_D(Y)} \quad (15)$$

The notation is such that  $\ln s/s' f(Y)$  is smaller than  $\ln s/s' f(X)$ . The fractionation favours D and T in the X compound. From Table I we note that  $\ln s/s' f_D(Y)/\ln s/s' f(X) - \ln s/s' f(Y)$  is of the order of unity unless Y is zero and the reactions is an exchange with H atoms. In this case  $\ln s/s' f_D(Y)/[\ln s/s' f_D(X) - \ln s/s' f_D(Y)]$  may be as low as 0.4. Since  $a-b < .11$ , we see from equation 15 that  $\ln \alpha_{T-H}/\ln \alpha_{D-H}$  is always less than 1.55. Thus, we have established the range of  $\ln \alpha_{T-H}/\ln \alpha_{D-H}$  to be 1.33–1.55 for equilibrium systems.

We now wish to consider the relative T—H and D—H fractionation in rate processes. Formally, we can write for the ratio of rate constants of isotopic molecules [15]

$$\ln (S_D S_H^\ddagger / S_H S_D^\ddagger) (k_H/k_D) = \ln (S_D/S_H) f_D - \ln (S_D^\ddagger/S_H^\ddagger) f_D^\ddagger (3n-7) + \ln (v_H^\ddagger/v_D^\ddagger) + T(u), \quad (16)$$

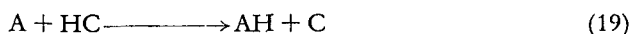
where  $T(u)$  is a correction for tunnelling and  $\ln v_H^\ddagger/v_D^\ddagger$  represents the relative frequencies of crossing of the barrier. If the tunnelling is small, then [15, 16]

$$-\ln (S_D^\ddagger/S_H^\ddagger) f_D^\ddagger (3n-7) + T(u) = -\ln (S_D^\ddagger/S_H^\ddagger) f_D^\ddagger (3n-6). \quad (17)$$

The relative T—H/D—H fractionation factor for rate processes then becomes in the small tunnelling approximation

$$\frac{\ln \alpha_{T-H}}{\ln \alpha_{D-H}} = \frac{\ln v_H^\ddagger/v_T^\ddagger + \ln \frac{S_T}{S_H} f_T - \ln \frac{S_T^\ddagger}{S_H^\ddagger} f_T^\ddagger (3n-6)}{\ln v_H^\ddagger/v_D^\ddagger + \ln \frac{S_D}{S_H} f_D - \ln \frac{S_D^\ddagger}{S_H^\ddagger} f_D^\ddagger (3n-6)} \quad (18)$$

The frequency ratios  $v_H^\ddagger/v_T^\ddagger$  and  $v_H^\ddagger/v_D^\ddagger$  can be calculated from the formula given by BIGEISEN and WOLFSBERG [17] for reactions of the type



$$v^\ddagger \sim \{a^2 (\mu_{H,D,T} + \mu_C) + \beta^2 (\mu_{H,D,T} + \mu_A) + 2a\beta \mu_{H,D,T}\}^{1/2}, \quad (20)$$

where  $\mu$  is the reciprocal mass and  $\beta/a$  determines the relative amount of bond formation to bond rupture. For a large range of values of  $\beta/a$  and  $\mu_A$  and  $\mu_C$  we find  $\ln v_H^\ddagger/v_T^\ddagger = (1.56-1.58) \ln v_H^\ddagger/v_D^\ddagger$ . For reactions involving hydrogen molecules the ratio is somewhat larger. Equation 18 then becomes

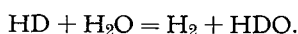
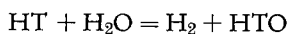
$$\frac{\ln \alpha_{T-H}}{\ln \alpha_{D-H}} = \frac{1.57 \ln (v_H^\ddagger/v_D^\ddagger) + a \ln \frac{S_D}{S_H} f_D - b \ln \frac{S_D^\ddagger}{S_H^\ddagger} f_D^\ddagger}{\ln (v_H^\ddagger/v_D^\ddagger) + \ln \frac{S_D}{S_H} f_D - \ln \frac{S_D^\ddagger}{S_H^\ddagger} f_D^\ddagger} \quad (21)$$

It is apparent from equation 21 that the behaviour of  $\ln \alpha_{T-H}/\ln \alpha_{D-H}$  for rate processes is quite similar to the behaviour for equilibrium processes. Since  $a$  and  $b$

are in the range 1.33—1.44 the frequency factor term  $\ln v_H^\ddagger/v_D^\ddagger$  serves to raise the limits of  $\ln a_{T-H}/\ln a_{D-H}$  of 1.33—1.55 found for equilibrium systems by a small amount. The amount depends in detail on the relative contribution of  $\ln v_H^\ddagger/v_D^\ddagger$  and  $\ln f/f^\ddagger$  to  $\ln a_{D-H}$ . At high temperatures  $\ln v_H^\ddagger/v_D^\ddagger$  is the dominant term, while at low temperatures  $\ln f/f^\ddagger$  is the dominant one.

### Applications of the theory

In the present paper we shall discuss several applications of the theory to fractionation processes involving water. First, we consider the exchange reactions



The experimental equilibrium constants for these reactions are each in quantitative agreement with theoretical computations. The values of  $\log K_T/\log K_D$  are therefore just those expected and are given in Table II.

TABLE II  
RELATIVE FRACTIONATION OF T AND D IN THE EXCHANGE OF  $H_2$ — $H_2O$

T°K	$\log K_T/\log K_D$
298	1.39
400	1.38
500	1.36
600	1.36

We now wish to consider the vapour pressures of the isotopic water molecules. AVINUR and NIR [18] have recently determined the relative vapour pressures of ( $H_2O/HTO$ ) and  $H_2O/HDO$ . They find that at 70°C and 100°C

$$\frac{a_T-1}{a_D-1} = \frac{\ln P_{H_2O}/P_{HTO}}{\ln P_{H_2O}/P_{HDO}} = 1.37 \pm 0.02.$$

In the theory of quantum corrections to the law of corresponding states [19], the vapour pressure has a quantum correction determined by the parameter  $A^{*2} = \hbar^2/\sigma^2 m \epsilon$ , where  $\sigma$  is the range of the inter-molecular force,  $m$  is the molecular weight, and  $\epsilon$  is the depth of the intermolecular potential. This theory has been successfully applied to the thermodynamic properties of the condensed rare gases. It leads to

$$\frac{a_T-1}{a_D-1} = \frac{A_{H_2O}^{*2} - A_{HTO}^{*2}}{A_{H_2O}^{*2} - A_{HDO}^{*2}} = \frac{\frac{1}{18} - \frac{1}{20}}{\frac{1}{18} - \frac{1}{19}} = 1.90,$$

which is in poor agreement with the experimental data. The  $A^{*2}$  correction to the law of corresponding states has been shown recently [13] to be inadequate for a variety of problems dealing with condensed phases of polyatomic molecules.

It has been shown that for vapour liquid equilibria [13] an equation similar to equation 11 applies. One obtains directly, therefore, from the theory of quantum effect in systems of polyatomic molecules  $(a_T-1)/(a_D-1) = 4/3$  which is in excellent agreement with experiment.

We turn to the fractionation of D and T in the electrolysis of water. This process is in current use in the determination of T in natural samples [8, 9, 20]. The basic difficulty with the method is the fact that the elementary enrichment factor is not reproducible, even in a given electrolytic cell. Deuterium enrichment is used as a monitor, and one obtains from the theory of the Raleigh distillation

$$\frac{X_T}{X_T^0} = \left( \frac{X_D}{X_D^0} \right)^{\alpha/\beta} \left( \frac{V^0}{V} \right)^{(\beta-\alpha)/\beta}, \quad (22)$$

where  $X$ 's are mol fractions,  $V$  is the volume and  $\beta$  and  $\alpha$  are the relative rates of electrolysis of  $\text{H}_2\text{O}/\text{HTO}$  and  $\text{H}_2\text{O}/\text{HDO}$  respectively. The data of KAUFMAN and LIBBY [8] support their hypothesis that  $\alpha_{\text{T-H}}/\alpha_{\text{D-H}}$  is a constant. The more recent experiments of ÖSTLUND and WERNER [20] definitely show that this ratio is a function of  $\alpha$ . We shall write equation 21 in the form

$$\frac{\ln \alpha_{\text{T-H}}}{\ln \alpha_{\text{D-H}}} = \gamma + \frac{\ln (\nu_D^*/\nu_T^*)/(\nu_H^*/\nu_D^*) - (\gamma - 1) \ln (\nu_H^*/\nu_D^*)}{\ln \alpha_{\text{D-H}}}, \quad (23)$$

where

$$\ln \left[ \left( \frac{S_T}{S_H} f_T \right) / \left( \frac{S_T^*}{S_H^*} f_T^* \right) \right] = \gamma \ln \left[ \left( \frac{S_D}{S_H} f_D \right) / \left( \frac{S_D^*}{S_H^*} f_D^* \right) \right]. \quad (24)$$

We assume  $\ln \frac{S_T^*}{S_H^*} f_T^* = \gamma \ln \frac{S_D^*}{S_H^*} f_D^*$ . Then, from Table I,  $\gamma$  is 1.38 for  $\text{H}_2\text{O}$  at 298 °K. The frequency ratios  $(\nu_H^*/\nu_T^*)$  and  $(\nu_H^*/\nu_D^*)$  are  $\sqrt{3}$  and  $\sqrt{2}$  respectively. These lead to

$$\frac{\ln \alpha_{\text{T-H}}}{\ln \alpha_{\text{D-H}}} = 1.38 + \frac{.06}{\ln \alpha_{\text{D-H}}}. \quad (25)$$

The value of  $\ln \alpha$  is about 2. Low apparent values of  $\alpha$  undoubtedly are a consequence of partial or complete equilibration of the hydrogen with the water. From equation 25 we obtain  $\ln \alpha_{\text{T-H}}/\alpha_{\text{D-H}} = 1.41$ , while the equilibrium value given in Table II is 1.39. From these we conclude  $\ln \alpha_{\text{T-H}}/\ln \alpha_{\text{D-H}} = 1.40 \pm 0.01$  in the electrolysis of water. The data of KAUFMAN and LIBBY give  $1.40 \pm .09$  while those of ÖSTLUND and WERNER cover the narrow range  $\log \alpha_{\text{T-H}}/\log \alpha_{\text{D-H}} = (1.35-1.41)$ . In the latter experiments  $\alpha$  varies from 4.2 to 11.9 and there is a systematic trend in  $\alpha_{\text{T-H}}/\alpha_{\text{D-H}}$  from 1.6 to 2.7. The theoretical results are in excellent agreement with experiment. It is clear that the enrichment of tritium should be calculated from the equation

$$\frac{\ln \alpha_{\text{T-H}}}{\ln \alpha_{\text{D-H}}} = \gamma$$

rather than from

$$\frac{\alpha_{\text{T-H}}}{\alpha_{\text{D-H}}} = \gamma'.$$

### Secondary isotope effects and tunnelling

Relative T—H vs. D—H isotope effects may be of some aid in the characterization of secondary isotope effects and the role of tunnelling in chemical reactions. It has been shown by WOLFSBERG [21] that secondary isotope effects can be represented in close approximation as pure temperature-dependent functions. Therefore, in the low-temperature region, i. e.  $u > 2\pi$ , the Swain approximation is appropriate and  $\ln (k_H/k_T)/\ln (k_H/k_D)$  will be close to 1.44. At high temperatures the ratio will

drop to 1.33, as given by equation 12. It is characteristic of secondary isotope effects that the temperature-independent frequency factor,  $(\nu_H^*/\nu_D^*)_{D,T}$ , is very close to unity. On the other hand, rate processes with small over-all isotope effects which arise primarily from the frequency factor will have values of  $\ln(k_H/k_T)/\ln(k_H/k_D)$  close to 1.57.

Reactions which proceed in part by tunnelling through the barrier should show an anomalously large rate for protium. Thus, the ratio  $\ln(k_H/k_T)/\ln(k_H/k_D)$  will be reduced from normal values if the tunnelling is larger than the  $u^2/24$  approximation. This may be a further tool for diagnosis of tunnelling in chemical reactions.

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# ОБЩИЕ ЗАКОНОМЕРНОСТИ, ОПРЕДЕЛЯЮЩИЕ ТЕРМОДИНАМИЧЕСКИЕ ИЗОТОПНЫЕ ЭФФЕКТЫ ПРИ ТРИТИЕВО-ПРОТИЕВОМ ОБМЕНЕ

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Abstract — Résumé — Аннотация — Resumen

## General rules governing thermodynamic isotope effects in tritium/protium exchange.

The marked difference between the mass of tritium and that of protium causes a significant difference in the chemical characteristics of these two isotopes of hydrogen, and, in particular, an extremely irregular distribution of tritium among hydrogenous substances during tritium-protium exchange.

The coefficients ( $\alpha$ ) of tritium distribution in various systems of hydrogenous substances are calculated by a method based on statistical thermodynamics, giving a quantitative measure of the thermodynamic isotope effect. It is shown that for some systems (containing hydrides of alkali metals) the value of  $\alpha$  may attain 20.

Lois générales régissant les effets isotopiques thermodynamiques accompagnant les échanges de tritium et de protium. Comme le tritium  $^3\text{H}$  et le protium  $^1\text{H}$  ont des masses très différentes, il en résulte des différences sensibles dans leurs propriétés chimiques, notamment une distribution très inégale du tritium entre les substances hydrogénées qui se manifeste pendant les échanges de ces deux isotopes de l'hydrogène.

Par la méthode de la thermodynamique statistique, l'auteur a calculé la valeur des coefficients ( $\alpha$ ) relatifs à la répartition du tritium dans divers systèmes de substances hydrogénées, ce qui permet de mesurer quantitativement l'effet isotopique thermodynamique. Il montre que pour certains de ces systèmes (sous l'influence d'hydrides de métaux alcalins)  $\alpha$  peut atteindre la valeur 20.

Общие закономерности, определяющие термодинамические изотопные эффекты при тритиево-протиевом обмене. Сильное различие масс трития и протия приводит к значительному различию химических свойств этих двух изотопов водорода и, в частности, к резко неравномерному распределению трития между водородо-содержащими веществами при тритий-протиевом обмене.

Методом статистической термодинамики вычислены значения коэффициентов ( $\alpha$ ) распределения трития в различных системах водородосодержащих веществ, являющихся количественной мерой термодинамического изотопного эффекта. Показано, что для некоторых систем (с участием гидридов щелочных металлов) значение  $\alpha$  может достигать двадцати.

Leyes generales que rigen los efectos isotópicos termodinámicos en el intercambio tritio-protio. Las masas del tritio y del protio son muy diferentes; por tanto las propiedades químicas de estos dos isótopos del hidrógeno difieren ampliamente, siendo, en particular, muy desigual la distribución del tritio en las sustancias hidrogenadas durante el intercambio tritio-protio.

Aplicando un método basado en los principios de la termodinámica estadística, se calcularon los valores de los coeficientes de distribución ( $\alpha$ ) del tritio en distintos sistemas de sustancias hidrogenadas; los datos así obtenidos permiten evaluar cuantitativamente el efecto isotópico termodinámico. El autor demuestra que para algunos sistemas (que contienen hidruros de metales alcalinos) el valor de  $\alpha$  puede alcanzar a 20.

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Интерес к реакциям изотопного обмена водорода обусловлен не только тем, что они лежат в основе химических методов концентриро-

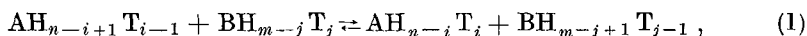
вания изотопов этого элемента. Обмен атома протия на атом трития (или дейтерия) является по существу простейшей химической реакцией замещения водорода, в результате которой химическое строение молекулы (в отличие от обычных химических реакций) существенно не меняется. Поэтому скорость перехода меченого атома водорода в определенных условиях может служить критерием реакционной способности водородосодержащего вещества.

Исследование реакций изотопного обмена водорода имеет три аспекта.

1. Термодинамическая (изотопно-равновесная) характеристика этих реакций;
2. Особенности кинетических законов, определяющих протекание обменных реакций, с учетом изотопных эффектов;
3. Природа и механизм обменной реакции.

Настоящий доклад посвящен первому из этих аспектов. В отличие от изотопов более тяжелых элементов в случае изотопов водорода должны проявляться значительные изотопные эффекты, обусловленные сильным относительным различием в массах и нулевых энергиях протия, дейтерия и трития. Действительно, как показывает опыт, при равновесии протиево-тритиевого обмена часто наблюдается довольно сильное отклонение распределения трития от равновероятностного. Это приводит к необходимости построения такой теории термодинамических изотопных эффектов, которая выявила бы общую закономерность, определяющую их величины и позволила заранее предвидеть численные значения коэффициентов распределения трития между различными химическими соединениями.

При изотопном обмене водорода между двумя водородосодержащими веществами  $\text{AH}_n$  и  $\text{BH}_m$  (где А и В части реагирующих молекул без атомов водорода) протекает не одна, а  $nm$  обменных реакций, любая из которых может быть выражена общим уравнением



где:  $i = 1, 2, 3 \dots n; \quad j = 1, 2, 3 \dots m.$

Для каждой из таких  $nm$  обменных реакций характерна своя константа равновесия, равная:

$$K_{ij} = \frac{[\text{AH}_{n-i} \text{T}_i][\text{BH}_{m-j+1} \text{T}_{j-1}]}{[\text{AH}_{n-i+1} \text{T}_{i-1}][\text{BH}_{m-j} \text{T}_j]}, \quad (2)$$

где величины, стоящие в скобках представляют собой равновесные концентрации соответствующих изотопных форм реагирующих компонентов.

Величина константы равновесия зависит, как известно, не только от различий в свойствах изотопов водорода, но также от соотношения чисел симметрии изотопных форм реагирующих веществ, и поэтому не может служить мерой термодинамического эффекта для системы в целом. В качестве такой меры удобно пользоваться коэффициентом



распределения ( $\alpha$ ) трития, который не зависит от симметрии реагирующих молекул. По определению, коэффициент распределения равен:

$$\alpha = \frac{([T]/[H]) \text{АН}_n}{([T]/[H]) \text{ВН}_m}, \quad (3)$$

где индексы  $\text{АН}_n$  и  $\text{ВН}_m$  означают компоненты, для которых берутся отношения равновесных концентраций трития и протия\*. При равновероятностном распределении изотопов в равновесии, т. е. при отсутствии термодинамического изотопного эффекта, величина  $\alpha$  равна единице. Чем больше термодинамический изотопный эффект, тем сильнее отличается  $\alpha$  от единицы.

Величины  $\alpha$  и  $K_{ij}$  однозначно связаны друг с другом. В работах [1—3] на примере дейтерообмена найдено соотношение между  $\alpha$  и  $K$ , позволяющее легко вычислять величину  $\alpha$  из константы равновесия суммарной реакции изотопного обмена



Согласно этому соотношению:

$$\alpha = K^{1/mn}. \quad (5)$$

где  $\alpha$ —коэффициент распределения трития, а  $K$ —константа равновесия реакции (4).

Следует отметить, что для вычисления  $\alpha$  может быть использована в принципе не только суммарная реакция (4), но и любая другая из протекающих в системе обменных реакций, описываемых уравнением (1). В случае обмена между компонентами, содержащими несколько атомов водорода, когда в системе протекает больше одной реакции, получающиеся значения  $\alpha$  будут точно равны друг другу только при условии равновероятностного распределения трития между разными изотопными формами одного и того же компонента. Как показывает опыт, в случае дейтерообмена это условие соблюдается с довольно хорошей точностью и значения  $\alpha$ , полученные из констант равновесия разных реакций не различаются сильнее чем на 5—6% (3). При проведении расчетов практически удобнее всего пользоваться, однако, суммарной реакцией, т. к. при этом отпадает необходимость иметь дело с частично замещенными изотопными формами. В случае обмена между компонентами с одним атомом водорода ( $m = n = 1$ ) единственная обменная реакция является суммарной. В этом случае коэффициент распределения трития численно совпадает с константой равновесия.

Таким образом, если известна величина  $K$  для суммарной реакции изотопного обмена, то пользуясь уравнением (5), можно определить значение  $\alpha$ . В то же время величину  $K$  можно вычислить из данных по колебательным спектрам реагирующих молекул с использованием метода статистической термодинамики. Согласно [4—6] выражение для константы равновесия  $K$  суммарной реакции (4) может быть записано в виде:

\* Величину  $\alpha$  для неравновесных систем следует называть коэффициентом распределения.

$$K = \frac{\left( \prod \frac{\omega_{AT_n}}{\omega_{AH_n}} \frac{1 - e^{-\frac{hc}{KT}\omega_{AH_n}}}{1 - e^{-\frac{hc}{KT}\omega_{AT_n}}} \right)^m e^{-\frac{hc}{2KT} m \sum (\omega_{AT_n} - \omega_{AH_n})}}{\left( \prod \frac{\omega_{BT_m}}{\omega_{BH_m}} \frac{1 - e^{-\frac{hc}{KT}\omega_{BH_m}}}{1 - e^{-\frac{hc}{KT}\omega_{BT_m}}} \right)^n e^{-\frac{hc}{2KT} n \sum (\omega_{BT_m} - \omega_{BH_m})}}, \quad (6)$$

где произведения и суммы берутся по всем основным колебательным частотам  $\omega$  см<sup>-1</sup> соответствующих молекул (с поправками на ангармоничность колебаний). Используя соотношение (5) и выражение (6), имеем:

$$\alpha = \frac{\left( \prod \frac{\omega_{AT_n}}{\omega_{AH_n}} \frac{1 - e^{-\frac{hc}{KT}\omega_{AH_n}}}{1 - e^{-\frac{hc}{KT}\omega_{AT_n}}} \right)^{1/n} e^{-\frac{hc}{2KT} \frac{1}{n} \sum (\omega_{AT_n} - \omega_{AH_n})}}{\left( \prod \frac{\omega_{BT_m}}{\omega_{BH_m}} \frac{1 - e^{-\frac{hc}{KT}\omega_{BH_m}}}{1 - e^{-\frac{hc}{KT}\omega_{BT_m}}} \right)^{1/m} e^{-\frac{hc}{2KT} \frac{1}{m} \sum (\omega_{BT_m} - \omega_{BH_m})}}. \quad (7)$$

Легко видеть, что числитель в выражении (7) зависит от частот колебания полностью тритированных ( $\omega_{AT_n}$ ) и не содержащих трития ( $\omega_{AH_n}$ ) молекул только одного компонента, а знаменатель — от соответствующих значений  $\omega_{BT_m}$  и  $\omega_{BH_m}$  для другого компонента. Таким образом величину  $\alpha$  можно представить как отношение двух величин  $\beta_1$  и  $\beta_2$ , каждую из которых можно вычислить из основных колебательных частот молекул данного водородосодержащего вещества, независимо от того, с каким веществом оно вступает в реакцию тритиевого обмена. Величину  $\beta$  мы называем  $\beta$ -фактором. Физический смысл  $\beta$ -фактора состоит в том, что он служит количественной мерой степени неравноценности протия и трития, проявляющейся в данном веществе.

Из формулы (7) легко видеть, что величина  $\beta$ -фактора любого водородосодержащего вещества, допустим  $AH_n$ , равна:

$$\beta = \left( \prod \frac{\omega_{AT_n}}{\omega_{AH_n}} \frac{1 - e^{-\frac{hc}{KT}\omega_{AT_n}}}{1 - e^{-\frac{hc}{KT}\omega_{AH_n}}} \right)^{1/n} e^{-\frac{hc}{KT} \frac{1}{n} \sum (\omega_{AT_n} - \omega_{AH_n})} \quad (8)$$

Индекс AT означает, что частота колебания относится к соединению, в котором все атомы водорода замещены на тритий.

Получение полностью тритированных соединений и экспериментальное измерение их колебательных спектров с целью определения основных частот колебания, необходимых для расчета  $\beta$ -факторов, представляет весьма сложную задачу. В настоящее время экспериментально определены основные колебательные частоты только для молекул  $T_2$  [5] и  $T_2O$  [8]. Вычисление частот колебания многоатомных тритированных молекул ( $\omega_{AT_n}$ ) путем простого деления соответствующих значений  $\omega_{AH_n}$  для этих же молекул на корень из отношения при-

веденных масс, не приводит к достаточно точным результатам из-за взаимодействия колебаний в сложных молекулах. Таким образом, отсутствие экспериментальных данных и невозможность их вычисления в случае многоатомных молекул водородосодержащих веществ, не позволяют вычислить  $\beta$ -факторы таких веществ, как это было сделано нами ранее для дейтеросоединений [3]. Поэтому мы предприняли расчет значений  $\beta$ -факторов двухатомных гидридов как одновалентных, так и поливалентных элементов.

Частоты колебаний полностью тритированных двухатомных гидридов\* вычисляли из экспериментальных частот колебания обычных гидридов простым делением их на корень из отношения приведенных масс, что вполне оправдано в случае двухатомных молекул, имеющих всего одну частоту колебания.

Расчет  $\beta$ -факторов вели по формуле (8) для температуры  $20^\circ\text{C}$ . Полученные значения  $\beta$   $20^\circ$  приведены в табл. I, в которой указаны также использованные при расчете значения частот колебания  $\omega_{\text{AH}}$  и  $\omega_{\text{AT}}$ . На рис. 1 наглядно показана зависимость  $\beta$ -фактора от поряд-

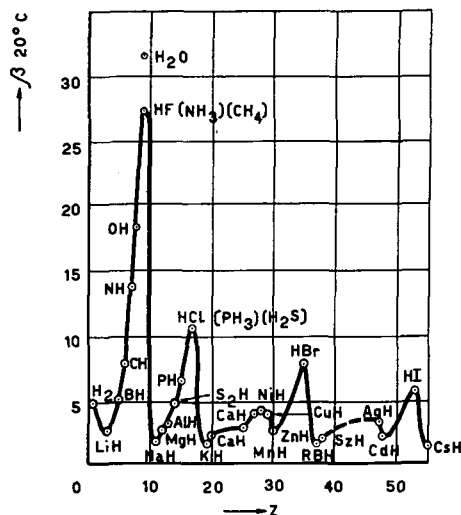


Рис. I Зависимость  $\beta$ -фактора от порядкового номера элемента, связанного с водородом.

кового номера элемента, связанного с водородом. Легко видеть, что эта зависимость носит периодический характер и напоминает соответствующую зависимость для силовых констант. Величина  $\beta$ -фактора двухатомного гидрида резко возрастает внутри каждого периода таблицы Менделеева по мере возрастания числа внешних электронов элемента, связанного с водородом. С другой стороны, при переходе от легких элементов к более тяжелым (при данном числе внешних электронов) внутри данной группы таблицы Менделеева  $\beta$ -факторы соответствующих гидридов постепенно уменьшаются. Сказанное отно-

\* В случае двухатомных гидридов поливалентных элементов (например, CH, NH, OH, SH и т.д.) речь идет о свободных радикалах.

ТАБЛИЦА I  
**ЧАСТОТА КОЛЕБАНИЯ ДВУХАТОМНЫХ ГИДРИДОВ И ТРИТИДОВ И  
 ЗНАЧЕНИЯ  $\beta$ -ФАКТОРОВ (20° C)**

Атомный номер	Элемент	Частота колебания, см <sup>-1</sup>		$\beta$ 20° C
		гидрида	тригида	
1	H	4154,65	878,0	4,8
3	Li	1359,2	878,0	2,7
5	B	2268	1417	5,0
6	C	2732	1694	1,8
7	N	3300	2029	13,7
8	O	3571,6	2180	18,3
9	F	3958,4	2397	27,4
11	Na	1132,9	680,6	1,9
12	Mg	1432,9	859,6	2,5
13	Al	1624,3	970,7	3,0
14	Si	2080	1242	4,6
15	P	2380	1417	6,3
17	Cl	2885,7	1711	10,5
19	K	964,5	570,7	1,7
20	Ca	1260	745,0	2,1
25	Mn	1580	928,7	2,9
27	Co	1890	1109	4,0
28	Ni	1926,6	1130,9	4,1
29	Cu	1866,0	1094,2	3,9
30	Zn	1497,3	877,5	2,7
35	Br	2559,3	1495,9	7,9
37	Rb	908,5	530,6	1,6
38	Sr	1172,2	684,4	2,0
47	Ag	1691,9	985,8	3,3
48	Cd	1338,1	779,4	2,3
53	J	2230,1	1297,6	5,1
55	Cs	875,5	509,3	1,5

ТАБЛИЦА II  
ЗНАЧЕНИЕ КОЭФФИЦИЕНТОВ РАСПРЕДЕЛЕНИЯ ТРИТИЯ ( $\alpha$  20° С)

Вещество	$\beta^* 20^\circ \text{C}$	Коэффициент распределения трития $\alpha 20^\circ \text{C}$														
		H <sub>2</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	HF	PH <sub>3</sub>	H <sub>2</sub> S	HCl	HBr <sub>2</sub>	HJ	ZiH	NaH	KH	RbH	CsH
H <sub>2</sub>	4,8	1	0,17	0,17	0,15	0,18	0,46	0,46	0,46	0,61	0,84	1,8	25	2,8	3,0	3,2
CH <sub>4</sub>	(27,6)	5,7	1	1	0,87	1,0	2,64	2,64	2,64	3,50	4,85	10,2	1,46	16,15	17,15	18,4
NH <sub>3</sub>	(27,6)	5,7	1	1	0,87	1,0	2,64	2,64	2,64	3,50	4,85	10,2	1,46	16,15	17,15	18,4
H <sub>2</sub> O	31,6	6,6	1,14	1,14	1	1,2	3,0	3,0	3,0	4,0	5,6	11,8	16,7	18,6	19,7	21,0
HF	27,4	5,7	1	1	0,87	1	2,6	2,6	2,6	3,46	4,8	10,2	14,4	16,0	17,1	18,3
PH <sub>3</sub>	(10,5)	2,2	0,38	0,38	0,33	0,39	1	1	1	1,33	1,84	3,9	5,5	6,2	6,6	7,0
H <sub>2</sub> S	(10,5)	2,2	0,38	0,38	0,33	0,39	1	1	1	1,33	1,84	3,9	5,5	6,2	6,6	7,0
HCl	10,5	2,2	0,38	0,38	0,33	0,39	1	1	1	1,33	1,84	3,9	5,5	6,2	6,6	7,0
HBr <sub>2</sub>	7,9	1,7	0,28	0,28	0,25	0,29	0,75	0,75	0,75	1	1,39	2,90	4,20	4,70	5,0	5,3
HJ	5,7	1,2	0,21	0,21	0,2	0,21	0,54	0,54	0,54	0,72	1	2,10	3,0	3,35	3,56	3,8
LiH	2,7	0,6	0,10	0,10	0,9	0,10	0,26	0,26	0,26	0,34	0,48	1	1,42	1,60	1,70	1,80
NaH	1,9	0,4	0,07	0,07	0,06	0,07	0,18	0,18	0,18	0,24	0,33	0,70	1	1,1	1,2	1,3
KH	1,7	0,36	0,06	0,06	0,06	0,05	0,15	0,15	0,15	0,22	0,30	0,63	0,90	1	1,1	1,1
RbH	1,6	0,33	0,06	0,06	0,06	0,05	0,15	0,15	0,15	0,21	0,28	0,60	0,85	0,94	1	1,1
CsH	1,5	0,30	0,05	0,05	0,05	0,05	0,14	0,14	0,14	0,20	0,26	0,56	0,80	0,88	0,94	1

\* В скобках даны значения  $\beta$ -фактора условно принятые равными  $\beta$ -факторам соответствующих галогидоводородов.

сится к двухатомным гидридам. Если величина  $\beta$ -фактора гидрида действительно однозначно определяется продолжением элемента в периодической таблице, а именно числом внешних электронов и числом внутренних электронных оболочек, то  $\beta$ -факторы многоатомных гидридов поливалентных элементов, относящихся к одному и тому же периоду таблицы Менделеева, не должны сильно отличаться друг от друга и должны быть близки по численному значению к  $\beta$ -фактору соответствующего голоидоводорода. Это объясняется тем, что молекулярные остатки, связанные только с одним атомом водорода в таких многоатомных гидридах изоэлектронны, а массы молекулярных остатков близки друг к другу и к массе атома голоида. Примером могут служить молекулы  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  и  $\text{HF}$ , остатки которых ( $\text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{OH}$  и  $\text{F}$ ) имеют по семь внешних электронов и обладают одинаковым числом внутренних электронов.

Эти основные положения закономерности, определяющей величину  $\beta$ -фактора были доказаны в случае дейтерообмена как расчетами [3], так и экспериментально (см. напр. [3, 7, 9, 10, 11]). Они же должны определять характер распределения трития при изотопном обмене водорода. Поэтому рядом с формулами голоидоводородов на рис. 1, в скобках, указаны формулы многоатомных гидридов, характеризующихся значением  $\beta$ -фактора, приблизительно равным его значению для этого голоидоводорода. В случае воды это подтверждается экспериментальными данными. Расчет  $\beta$ -фактора  $\text{T}_2\text{O}$ , для которой, как указывалось выше, известны все четыре частоты с поправками на ангармоничность колебаний [8], дал величину  $\beta^{\text{H}_2\text{O}} 20^\circ = 31,6$ , которая близка к значению  $\beta^{\text{HF}} 20^\circ = 27,4$ .

В табл. II приведены значения коэффициентов распределения  $\alpha$   $20^\circ$ , отвечающие равновесию противо-третиевого обмена между всевозможными парами водородосодержащих веществ. Эти значения  $\alpha$ , полученные как частное от деления соответствующих  $\beta$ -факторов, характеризуют максимально возможные в природе термодинамические изотопные эффекты (при  $20^\circ$ ).

### Выводы

1. Вычислены значения  $\beta$ -факторов для двухатомных и многоатомных гидридов и значения коэффициентов распределения трития  $\alpha$   $20^\circ$  между различными парами водородосодержащих веществ.

2. Результаты расчета подтверждают общую закономерность равновесного распределения трития при изотопном обмене водорода, позволяющую заранее предвидеть величины  $\alpha$  для любых пар водородосодержащих веществ.

3. Показано, что максимально возможный термодинамический изотопный эффект, должен наблюдаться при противо-третиевом обмене в системах, включающих, с одной стороны, гидрид по возможности более тяжелого щелочного металла, а с другой стороны гидрид какого-нибудь неметалла из первого периода системы элементов, например углеводород, аммиак, воду, фтористый водород (или же вещество, содержащее C-H, N-H или OH-связи). Равновесие при обмене протия и трития в таких системах должно характеризоваться значениями  $\alpha$   $20^\circ$ , близкими к двадцати.

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# THE DETERMINATION OF SUB-MICROGRAM QUANTITIES OF AMINO ACIDS WITH $H^3$ - AND $C^{14}$ -LABELLED 1-FLUORO-2,4 DINITRO-BENZENE

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Abstract — Résumé — Аннотация — Resumen

**The determination of sub-microgram quantities of amino acids with  $H^3$ - and  $C^{14}$ -labelled 1-fluoro-2,4 dinitrobenzene.** A method of isotope derivation analysis is described for the estimation of amino acids at levels as low as  $10^{-5}$   $\mu M$  in protein hydrolysates.

1-fluoro-2,4-dinitrobenzene- $H^3$  (G) was synthesized from bromobenzene- $H^3$  (G), and 1-fluoro-2,4-dinitrobenzene- $C^{14}$  (G) was prepared from chlorobenzene- $C^{14}$  (G).

The method of analysis involves the treatment of the mixture of amino acids with the tritiated reagent (specific activity 12,8  $\mu c/\mu$ -equivalent) in alkaline solution followed by the addition of known activities (6000 dpm) of  $C^{14}$ -labelled 2,4-dinitro phenyl derivatives. After solvent extraction the reaction mixture is separated into its constituent dinitro phenyl derivatives by two-way paper chromatography, and the  $H^3$  and  $C^{14}$  contents of each spot are determined by combustion and gas counting. The  $H^3$  count gives a measure of the amount of DNP derivative of amino acid isolated from the original mixture, and the  $C^{14}$  count gives a measure of losses incurred during the analysis.

The results obtained from the analysis of  $\mu g$  of hydrolyzed insulin are in good agreement with values obtained by derivative analysis with  $H^3$  and  $C^{14}$ -labelled acetic anhydride and by ion exchange resin chromatography.

**Détermination d'acides aminés en quantités inférieures au microgramme à l'aide de 1-fluoro-2,4-dinitrobenzène marqué au  $^3H$  et au  $^{14}C$ .** Les auteurs décrivent une méthode d'analyse par dérivation isotopique permettant d'évaluer des quantités d'acides aminés aussi faibles que  $10^{-5}$   $\mu M$  dans des hydrolysats de protéine.

Le 1-fluoro-2,4-dinitrobenzène- $^3H$  (G) a été préparé par synthèse à partir du bromobenzène- $^3H$  (U), et le 1-fluoro-2,4-dinitrobenzène- $^{14}C$  (G) à partir du chlorobenzène- $^{14}C$  (U).

Cette méthode d'analyse implique le traitement du mélange d'acides aminés par le réactif tritié (activité spécifique: 12,8  $\mu c$  par microéquivalent) en solution alcaline, suivi de l'addition de dérivés du dinitro-2,4-phényle marqué au  $^{14}C$  d'activité connue (6000 dpm). Après extraction par solvant, les dérivés du dinitro-phényle contenus dans le mélange résultant de la réaction sont séparés par chromatographie bidimensionnelle sur papier; la teneur en  $^3H$  et  $^{14}C$  de chaque tâche est déterminée combustion et comptage en phase gazeuse. Le comptage de  $^3H$  permet d'évaluer la quantité de dérivés DNP (dinitro-phényle) de l'acide aminé qui a été isolée du mélange initial, et celui du  $^{14}C$  indique les pertes survenues durant l'analyse.

Les résultats obtenus par l'analyse d'un microgramme d'insuline hydrolysée concordent avec les valeurs que donne l'analyse par dérivation à l'aide d'anhydride acétique marqué au  $^3H$  et  $^{14}C$ , et avec celles que fournit la chromatographie par échange d'ions.

**Подсчет суьмикрограммных количеств аминокислот при помощи 2 : 4 динитрофторьбензола, меченного  $H^3$  и  $C^{14}$ .** Описывается метод изотопного деривационного анализа для определения аминокислот при низком уровне в  $10^{-5}$  микро-моль в гидролизатах протеина.

2 : 4 динитрофторьбензола- $H^3$  (G) был синтезирован из бромбензола- $H^3$ (G) и 2 : 4 динитрофторьбензола- $C^{14}$ (G), который был получен из хлорбензола- $C^{14}$ (G).

Метод анализа включает обработку смеси amino-кислот тритированным реактивом (удельная активность 12.8 микро кюри/микро эквивалент) в щелочном

растворе, к которому присоединяется примесь с известной активностью (6000 распадов в минуту) производных 2 : 4 динитрофенила, меченного  $C^{14}$ . После растворяющей экстракции смешанная реакция выделяет из своего состава производные динитрофенила двумя путями хроматографии на бумаге и содержание  $H^3$  и  $C^{14}$  каждой капли определяется сжиганием и газовым подсчетом. Подсчет  $H^3$  дает количество, равное производной ДНК из аминокислоты, отделенной от основной смеси, а счет  $C^{14}$  указывает на величину потерь, получившихся во время анализа.

Итоги, полученные в результате анализа 1 микрограмма гидролизованного инсулина полностью согласуются с величинами, полученными в результате деривационного анализа с использованием уксусного ангидрида, меченного  $H^3$  и  $C^{14}$  и с помощью хроматографии ионного обмена смол.

**Determinación de cantidades de aminoácidos inferiores al microgramo por medio de 1-fluoro-2,4-dinitrobenceno marcado con  $^3H$  y  $^{14}C$ .** La memoria describe un método de análisis por derivación isotópica que sirve para determinar cuantitativamente aminoácidos en cantidades del orden de  $10^{-5}$  micromoles en hidrolizados de proteínas.

Los autores sintetizaron el 1-fluoro-2,4-dinitrobenceno- $^3H$  (G) a partir de bromobenceno- $^3H$  (G), y el 1-fluoro-2,4-dinitrobenceno- $^{14}C$  (G) a partir de clorobenceno- $^{14}C$  (G).

Según este método de análisis, la mezcla de aminoácidos se trata con el reactivo tritiado (actividad específica 12,8  $\mu\text{C}/\text{microequivalente}$ ) en solución alcalina, añadiendo seguidamente actividades conocidas (6000 dpm) de derivados 2,4-dinitrofenílicos marcados con  $^{14}C$ . Después de la extracción con disolventes, los derivados dinitrofenílicos presentes en la mezcla se separan por cromatografía bidimensional sobre papel y los contenidos en  $^3H$  y en  $^{14}C$  de cada mancha se determinan por combustión y recuento con ayuda de un contador de gas. El recuento del  $^3H$  indica la cantidad del derivado dinitrofenílico del aminoácido aislado de la mezcla inicial, y el recuento del  $^{14}C$  constituye una medida de las pérdidas que se producen durante el análisis.

Los resultados obtenidos al analizar 1  $\mu\text{g}$  de insulina hidrolizada concuerdan satisfactoriamente con los valores que suministra el análisis por derivación empleando anhídrido acético marcado con  $^3H$  y con  $^{14}C$ , y con los que se obtienen mediante cromatografía de intercambio iónico.

## Introduction

1-fluoro-2,4-dinitrobenzene (FDNB) was first used for the preparation of 2,4-dinitrophenyl derivatives of amino acids (DNP amino acids) by SANGER [1] in his investigation of the N-terminal groups of insulin. This reagent has now become widely used not only for protein end-group analysis but also for the determination of amino acids in protein hydrolysates. The techniques employed depend on the quantitative separation of the DNP derivatives and their subsequent estimation. Methods of preparation and chromatographic separation of DNP-amino acids have recently been reviewed [2]; and procedures for their titrimetric [3], colorimetric [1] and spectrophotometric [4] estimation have been described. The most sensitive of the non-isotope methods is capable of measuring 0.1  $\mu\text{M}$  of an amino acid.

In recent years this laboratory has been concerned with the development of analytical techniques for the estimation of sub-microgram quantities of amino acids for the study of the protein composition and free amino acid content of small groups of cells undergoing carcinogenesis. A method of isotope derivative analysis employing  $H^3$ - and  $C^{14}$ -labelled acetic anhydrides as reagents for the assay of amino acids has been described by WHITEHEAD [5]. This technique permits measurement of  $10^{-5}$   $\mu\text{M}$  of an amino acid, but the use of N-acetyl derivatives has a number of disadvantages which will be discussed later. The purpose of this paper is to describe the development of the same basic technique to produce a more

advantageous method by the use of 1-fluoro-2,4-dinitrobenzene- $H^3$ -(G) ( $H^3$ FDNB) and 1-fluoro-2,4-dinitrobenzene- $C^{14}$ -(G) ( $C^{14}$ -FDNB) as the labelled reagents.

## Experimental

### PREPARATION OF INERT DNP-AMINO ACIDS

Unlabelled derivatives that were required in the early stages of the work were prepared by the methods reviewed by BISERTE *et al.* [2].

### PREPARATION OF LABELLED COMPOUNDS

The preparation of labelled compounds was carried out in a highly efficient draught cupboard with all the usual precautions for handling radioactive materials. The apparatus used was of the standard type for small-scale organic synthetic operations with interchangeable glass joints; and, when necessary, a high vacuum manifold of conventional design was employed. All apparatus was decontaminated after use by immersion in acetone, washing with water, immersion in potassium dichromate-sulphuric acid cleaning mixture and, finally, continued washing with water.

#### 1-chloro-2,4-dinitrobenzene- $C^{14}$ -(G)

Chlorobenzene- $C^{14}$ (G) (0.15 mM, 0.15 mc) was diluted to 5.0 mM (0.56 g) with inactive chlorobenzene and nitrated in a 10 ml flask with 2.0 ml concentrated sulphuric acid and 2.0 ml of fuming nitric acid. The reaction mixture was then heated under reflux on a boiling-water bath for 1 h, cooled and poured onto crushed ice. The crude product was melted three times under water, allowed to solidify and filtered on a water pump, to be finally recrystallized from aqueous alcohol. The yield was 0.94 g (94% theory).

#### 1-fluoro-2,4-dinitrobenzene- $C^{14}$ -(G)

The 1-chloro-2,4-dinitrobenzene- $C^{14}$ -(G) prepared above was converted to the analogous 1-fluoro compound by the method described by SAUNDERS *et al.* [6] for the preparation of the inert reagent.

The labelled 1-chloro compound was dissolved in 0.98 g nitrobenzene, and 0.55 g potassium fluoride was added. The reaction mixture was heated at 205–210 °C on an oil bath for 5 h, cooled, filtered and the residue washed with  $3 \times \frac{1}{2}$  ml portions of ether. The filtrate and washings were evaporated on a high vacuum manifold to give a solution of the required  $C^{14}$ -FDNB in nitrobenzene. The yield of solution was 1.60 g, which, after subtraction of the nitrobenzene added, is equivalent to 0.70 g (81% theory) of the required compound.

The 1-fluoro-2,4-dinitrobenzene- $C^{14}$ -(G) could be separated from the nitrobenzene by means of a silica gel column eluted with a 1:1 ether: petroleum ether mixture. However, since the presence of nitrobenzene had no adverse effect on the subsequent preparation of  $C^{14}$ -labelled DNP derivatives, separation was considered to be unnecessary.

#### 1-bromo-2,4-dinitrobenzene- $H^3$ -(G)

Bromobenzene- $H^3$ (G) (1.0 mM, 100 mc) was diluted to 5.0 mM (0.78 g) with inactive bromobenzene and nitrated with 2.0 ml concentrated sulphuric acid and 2.0 ml fuming nitric acid on a boiling water bath for 1 h. The reaction mixture

was processed as described above for the labelled 1-chloro compound to give 1.11 g (91% theory) of 1-bromo-2,4-dinitrobenzene- $H^3$ (G).

#### *1-fluoro-2,4-dinitrobenzene- $H^3$ -(G)*

The 1-bromo compound prepared above was converted into the required  $H^3$ -FDNB by exactly the same procedure as given for  $C^{14}$ -FDNB, except that a temperature of 190–195 °C was used. The yield of  $H^3$ -FDNB in nitrobenzene solution was 1.77 g equivalent to 0.79 g (94% theory) of labelled reagent.

The 1-fluoro-2,4-dinitrobenzene- $H^3$ -(G) could be separated from the nitrobenzene and unchanged 1-bromo compound with a column as in the purification of  $C^{14}$ -FDNB. The presence of nitrobenzene has no effect on the preparation of  $H^3$ -DNP derivatives; and, since traces of unchanged 1-bromo-2,4-dinitrobenzene- $H^3$ -(G) having the same equivalent specific activity as the  $H^3$ -FDNB could only react to give DNP derivatives of the same equivalent specific activity, purification was again considered to be unnecessary.

#### *$C^{14}$ -labelled dinitrophenyl amino acids*

The method used by LEVY *et al.* [7] for preparing inert compounds was adapted to produce most of the labelled derivatives on the milligram scale.

The amino acid (5.0 mg) was placed in a 5.0 ml flat-bottomed B10 stoppered tube; and 1.0 ml of water was added, followed by 10 mg of sodium carbonate and 20  $\mu$ l of  $C^{14}$ -FDNB in nitrobenzene solution. The reaction mixture was stirred at 40 °C by means of a micromagnetic stirrer for 1 h. It was then extracted with 2  $\times$  1 ml of ether in the reaction tube by micro-pipetting, and the extracts were discarded. The remaining aqueous solution was acidified with dilute hydrochloric acid and extracted with 2  $\times$  1 ml of ether by the same technique. The ether extract was evaporated to dryness, and the residue was taken up in 5.0 ml 50% aqueous acetone or N/20 sodium bicarbonate solution, depending on the solubility of the labelled derivative.

The purity of the labelled compound was checked by chromatography, and any active dinitrophenol contaminant was removed by acidifying the solution if necessary, evaporation of it to dryness *in vacuo* and heating the residue at 70 °C on a high vacuum manifold. However, this treatment was rarely required.

$C^{14}$ -labelled di-DNP-tyrosine, di-DNP-lysine, di-DNP-histidine and DNP-arginine were best prepared by adaption of the method of RAO *et al.* [8] in a manner similar to that described above.

In this procedure the reaction was carried out in 50% aqueous ethanol solution, and sodium bicarbonate was used instead of carbonate. It was necessary to evaporate off the ethanol *in vacuo* before extraction of the reaction mixture with ether. The histidine and arginine derivatives were extracted from the acidified aqueous solution with *n*-butanol.

#### STANDARDIZATION OF 1-FLUORO-2,4-DINITROBENZENE- $H^3$ -(G)

A standardized solution of leucine (0.54  $\mu$ g/ml) was obtained and 0.1 ml was measured into a 5.0 ml reaction tube. Sodium carbonate solution (1.0 ml, 0.1%) was added followed by 5  $\mu$ l of  $H^3$ -FDNB solution; and the mixture was stirred on a micromagnetic stirrer at 40 °C for 1 h. To the reaction mixture was then added a known activity (approximately 6000 dpm, 10  $\mu$ g) of  $C^{14}$ -DNP-leucine, and the mixture was thoroughly shaken and extracted with 3  $\times$  1 ml of ether by micro-

pipetting in the reaction tube. The aqueous phase was then acidified with dilute hydrochloric acid and extracted with  $2 \times 1$  ml ether, and the ether extract was evaporated to dryness *in vacuo*.

The residue was taken up in acetone ( $2 \times 0.5$  ml) and chromatogrammed on Whatman No. 2 paper by ascending technique in toluene; pridine: 2-chlorethanol: 0.8N aqueous ammonia (30:9:18:18) [4]. The yellow chromatogram spot was excised and assayed for  $H^3$  and  $C^{14}$  by combustion and gas counting technique, as described by WHITEHEAD [5].

Confirmatory determinations were carried out with standardized solutions of valine, alanine and glycine.

#### ESTIMATION OF AMINO ACIDS IN A SYNTHETIC MIXTURE

A solution containing known amounts of leucine, valine, alanine and glycine was prepared, and 0.1 ml (approximately  $0.2 \mu\text{g}$  of total amino acid) was reacted with 0.1 ml sodium carbonate solution (1%) and  $5 \mu\text{l}$  of  $H^3$ -FDNB solution at  $40^\circ\text{C}$  for 1 h with a micromagnetic stirrer after the addition of  $C^{14}$ -DNP-leucine,  $C^{14}$ -DNP-valine,  $C^{14}$ -DNP-alanine and  $C^{14}$ -DNP-glycine (6000 dpm,  $10 \mu\text{g}$  for each derivative); the same extraction procedure was followed as in the standardization. The dry residue from the final ether extract was taken up in acetone ( $2 \times 0.5$  ml) and applied to Whatman No. 2 paper. A two-dimensional chromatogram was then run with the "toluene" system followed by a "phosphate" system ( $\text{NaH}_2\text{PO}_4$ :  $\text{Na}_2\text{HPO}_4$ , 2:1, 1.5 M, pH 6.0) used in descent. The yellow chromatogram spots were excised and assayed for  $H^3$  and  $C^{14}$  content by gas counting.

A similar estimation was performed with a solution of proline, serine, tyrosine and phenylalanine, except that the reaction was carried out in 50% aqueous ethanal solution for 2 h and sodium bicarbonate replaced the sodium carbonate. After addition of known activities of  $C^{14}$ -DNP derivatives of the amino acids under investigation, it was necessary to remove the alcohol *in vacuo* before proceeding with the extraction.

#### ESTIMATION OF AMINO ACIDS IN A PROTEIN HYDROLYSATE

Insulin was hydrolyzed as described by WHITEHEAD [5]. Ethanol (1.0 ml) was added to 1.0 ml of the hydrolysate (equiv.  $0.90 \mu\text{g}$  insulin), and this was reacted with 1.0 mg sodium bicarbonate and  $5 \mu\text{l}$  of  $H^3$ -FDNB solution at  $40^\circ\text{C}$  for 2 h. Known activities of  $C^{14}$ -DNP derivatives of the amino acids being estimated were added, and after thorough shaking the ethanol was removed *in vacuo*. The remaining aqueous reaction mixture was extracted, chromatogrammed and assayed, as for the synthetic mixture.

The estimation of histidine and arginine required an additional extraction of the acidified aqueous phase with  $2 \times 1$  ml n-butanol. This extract was evaporated *in vacuo* and chromatogrammed separately in one dimension with the "phosphate" system.

#### THE DETERMINATION OF N-TERMINAL GROUPS

The method of SANGER [1] was adapted to the microgram level. Ethanol (1.0 ml) was added to 1.0 ml of an aqueous solution of insulin ( $1.80 \mu\text{g}/\text{ml}$ ) and this was reacted with 1 mg sodium bicarbonate and  $5 \mu\text{l}$  of  $H^3$ -FDNB solution under the usual conditions. Known activities of  $C^{14}$ -DNP-phenyl alanine and  $C^{14}$ -DNP-glycine were added and the mixture thoroughly shaken. The ethanol was removed

*in vacuo*, and the remaining aqueous reaction mixture was extracted with  $3 \times 1$  ml ether. Concentrated hydrochloric acid (1.0 ml) was then added to the aqueous phase, and the solution was refluxed for 8 h.

The resulting hydrolysate was extracted with  $2 \times 1$  ml ether, the extract evaporated to dryness *in vacuo* and the residue chromatogrammed with the "toluene" and "phosphate" systems. The yellow chromatogram spots were excised and assayed for  $H^3$  and  $C^{14}$  content by combustion and gas counting.

## Results

Table I shows the values obtained for the specific activity of the 1-fluoro-2,4-

TABLE I  
STANDARDIZATION OF 1-FLUORO-2: 4-DINITRO BENZENE- $H^3$ -(G)

Amino acid used	Weight taken ( $\mu$ g)	Molecular weight	Activity $C^{14}$ -DNP-deriv. added (dpm)	Activity $C^{14}$ -DNP-deriv. recovered (%)	Activity $H^3$ -DNP-deriv. recovered ( $\mu$ c $\cdot 10^{-3}$ )	Specific activity of reagent ( $\mu$ c/ $\mu$ M)
Leucine	0.054	131	6474	45.2	2.319	12.45
Valine	0.025	117	5957	40.7	1.131	13.00
Alanine	0.061	89	5032	45.4	4.033	12.96
Glycine	0.025	75	4565	48.1	2.063	12.87
						mean $12.82 \pm 1\%$ S.D.

dinitrobenzene- $H^3$ -(G). It will be seen that the standard deviation from the mean is only 1%.

The results of the determination of amino acids in synthetic mixtures are given in Table II. These results show the validity of the technique to within  $\pm 5\%$  in nearly all cases.

TABLE II  
ESTIMATION OF AMINO ACIDS IN SYNTHETIC MIXTURES

Amino acid	Amount taken ( $\mu$ g)	Amount observed ( $\mu$ g)	Error (%)	Recovery of $C^{14}$ activity added (%)
Leucine	0.054	0.055	+ 1.8	20
Valine	0.050	0.050	0.0	25
Alanine	0.061	0.063	+ 3.3	27
Glycine	0.050	0.048	- 4.0	52
Proline	0.033	0.032	- 3.0	28
Serine	0.075	0.078	+ 4.0	36
Phenylalanine	0.027	0.025	- 7.5	31
Tyrosine	0.068	0.070	- 2.9	15

Table III gives the figures obtained for the composition of insulin. All the values lie within 4% of those expected from the structure of insulin given by RYLE *et al.* [9], and the accuracy appears to be more consistent than that obtained in the acetyl

TABLE III  
DETERMINATION OF AMINO ACIDS IN HYDROLYSATE FROM BOVINE INSULIN

Method	Isotopic DNP method		Isotopic acetyl method		Spectrophotometric DNP method		Ion exchange resin method		
Amount of insulin used	(1 $\mu$ g)		(2 $\mu$ g)		(1 mg)		(2 mg)		
	Amount found ( $\mu$ g/100 $\mu$ g of protein)	Difference from calc. amount present (%)	Amount found ( $\mu$ g/100 $\mu$ g of protein)	Difference from calc. amount present (%)	Amount found ( $\mu$ g/100 $\mu$ g of protein)	Difference from calc. amount present (%)	Amount found ( $\mu$ g/100 $\mu$ g of protein)	Difference from calc. amount present (%)	Calc. amount present ( $\mu$ g/100 $\mu$ g protein)
Leucines	16.5	+ 3.1	16.1	+ 0.6	16.3	+ 1.9	14.9	- 6.9	16.0
Valine	10.4	+ 2.0	12.0	+ 17.6	9.4	- 7.8	9.6	- 5.9	10.2
Alanine	4.6	- 2.1	4.9	+ 4.2	4.7	0.0	4.7	0.0	4.7
Glycine	5.1	- 1.9	5.3	+ 1.5	5.5	+ 5.8	5.2	0.0	5.2
Serine	5.7	+ 3.6	5.7	+ 3.6	4.2	- 23.6	4.8	- 12.7	5.5
Threonine	2.0	- 4.8	2.1	0.0	2.1	0.0	1.9	- 10.0	2.1
Phenylalanine	9.1	+ 4.7	9.0	+ 4.0	8.7	0.0	8.7	0.0	8.7
Tyrosine	12.6	0.0	13.3	+ 5.5	12.0	- 5.0	12.6	0.0	12.6
Proline	2.0	0.0	2.3	+ 10.0	2.1	0.0	2.3	+ 10.0	2.1
Lysine	2.6	0.0	2.7	+ 3.8	2.6	0.0	2.6	0.0	2.6
Glutamic acid	10.1	- 1.0	10.6	+ 2.9	10.3	0.0	10.3	0.0	10.3
Arginine	3.5	+ 2.9	—	—	3.4	0.0	3.4	0.0	3.4
Histidine	5.6	+ 3.7	—	—	5.1	- 5.0	5.4	0.0	5.4

derivative technique of WHITEHEAD [5]. The results as a whole are in good agreement with those reported by HARFENIST [10] using ion-exchange resin chromatography on the hydrolysate from 2 mg of insulin. The values also agree with the ones given by LEVY [4]), who used spectrophotometric measurements on the DNP derivatives of the hydrolysate from 1.0 mg of protein.

The values for the end group analysis are shown in Table IV, and again there is good agreement with those expected from theory.

TABLE IV  
DETERMINATION OF N-TERMINAL GROUPS OF INSULIN

Amino acid	Amount of insulin taken ( $\mu$ g)	Amount of N-terminal amino acid found ( $\mu$ g)	Number of residues found	Number of residues present**
Glycine	1.80	0.024	1.02	1
Phenylalanine	1.80	0.038	1.34	1

Determination of N-Terminal Group of Ribonuclease

Amino acid	Amount of ribonuclease taken ( $\mu$ g)	Amount of N-terminal amino acid found ( $\mu$ g)	Number of residues found	Number of residues present*
Lysine	1.96	0.025	1.18	1

\* Number of residues calculated from formula of RYLE *et al.* [9].

\*\* Number of residues calculated from formula of REDFIELD and ANFISEN.

## Discussion

The use of  $H^3$ - and  $C^{14}$ -labelled 1-fluoro-2,4-dinitrobenzene provides a method for estimation of amino acids and N-terminal groups in 1  $\mu$ g of protein with an accuracy at least as good as that obtained by the established non-isotopic methods, which require as much as 1.0 mg protein.

The sensitivity of isotopic derivation analysis is dependent on the specific activity of the reagent used. Tritium is an ideal isotope for this work because it is readily available at very high activity, it has a relatively long half-life, and labelled reagents are easily synthesized.

An advantage of the isotope method is the independence of results on losses in procedures following the addition of the labelled derivative, provided enough derivative remains for the final counting. For a reagent of given activity the accuracy of the method is raised by high recoveries. Dinitrophenyl derivative analysis has greater accuracy than does acetyl derivative analysis; because, with the use of reagents of similar equivalent activity, higher recoveries are obtained in the former method.

Dinitrophenyl derivative analysis has several other advantages over the acetyl method. End-group analysis as well as amino-acid analysis can be achieved. Chromatographic resolution is better and more reproducible. Chromatogram spots are self-indicating, while in the case of acetyl derivatives visualization is extremely difficult. Dinitrophenylation and subsequent manipulation of labelled derivatives is much simpler and less time-consuming. The labelled reagents and derivatives used



in the dinitrophenyl method when excluded from light are far more stable than those used in the acetyl method and therefore require much less restandardization.

### ADDENDUM

Since the submission of this paper the method of N-Terminal group analyses has been applied to Ribonuclease. The results obtained are now included in Table IV.

A method of C-Terminal group analysis has also been developed by modifying the macro technique of NIU and FRAENKEL-CONRAT [12] to the microgram scale.

3—4  $\mu\text{g}$  protein and 5  $\mu\text{l}$  hydrazine (98%, distilled from BaO) were heated in an evacuated sealed tube at 100°C for 4 hr. The tube was opened, excess hydrazine removed *in vacuo*, and the residue taken up in 0.5 ml water. The solution was shaken with 0.1 ml benzaldehyde and the aqueous layer removed by micro-pipetting. The benzaldehyde layer was washed in  $3 \times 0.1$  ml water and the amino acid composition of the combined aqueous layer and washings was determined using DNP derivative analysis.

The results obtained for the C-Terminal groups of insulin and ribonuclease are shown in Table V.

TABLE V  
DETERMINATION OF THE C-TERMINAL GROUPS OF INSULIN

Amino acid	Amount of insulin taken ( $\mu\text{g}$ )	Amount of C-terminal amino acid found ( $\mu\text{g}$ )	Number of residues found	Number of residues present*
Alanine	3.6	0.042	0.76	1
Asparic acid**	3.6	0.039	0.47	0

Determination of the C-Terminal Group of Ribonuclease

Amino acid	Amount of ribonuclease taken ( $\mu\text{g}$ )	Amount of C-terminal amino-acid found ( $\mu\text{g}$ )	Number of residues found	Number of residues present***
Valine	3.92	0.031	0.92	1

\* Number of residues calculated from formulae. RYLE *et al.* [9].

\*\* Aspartic acid was present due to hydrolysis of C-Terminal asparagine.

\*\*\* Number of residues calculated from formulae. REDFIELD and ANFINSEN [11].

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## DISCUSSION XII

**R. Glascock** (United Kingdom): I would like to congratulate the authors on their very accurate method of analysis but also to ask whether an error of not more than 2% — the error claimed is 1.9% — reflects the overall accuracy of their method. I have always found that, in determinations of radioactivity, a reproducibility of  $\pm 1.5\%$  is quite satisfactory. Since the authors are claiming a total error of not more than 2%, I should like to ask what is the reproducibility of their radioassay method.

**D. Beale** (United Kingdom): I should mention at the outset that this paper was not intended as a detailed report on our counting techniques and on tests of the efficiency and reproducibility of our counting. We used exactly the same counting set-up and techniques that Dr. Whitehead described in his original papers, with which I believe Dr. Glascock is quite familiar. The question as to our error apparently refers to Table 3, on the hydrolysis of insulin. I have added up the error values and the result is a mean difference of 1.9% which, as Dr. Glascock implies, is quite surprising. Of course, this is really not a rigorous system for dealing with the results but just an approximate means of comparing the two methods: the DNP isotopic method and the acetyl isotopic method. I think one should pay more attention to the actual errors obtained in the case of each particular amino acid, which, as you can see from Table III, include such values as +3.1, +2, -4.8, +4.7%. It is true that there are three values of 0% and a value of -1, but of course this is purely an interrelationship of errors. In the case of the 0 value, of course this is purely an interrelationship of errors. In the case of the 0% value, for example, our counting error for  $H^3$  could have been -2% down and the error in our recovery measurement for  $C^{14}$  +2% up and this would have given us an overall value of 0%. I think that this is the sort of thinking that happens. Examination of the actual individual error for each particular case shows, generally speaking, that the values obtained with DNP method are more consistent than those with the acetyl method.

**J. K. Whitehead** (United Kingdom): As co-author of this paper, I might add to what Mr. Beale has said. In reply to Dr. Glascock's question, we always had a total count of at least 10 000 by our technique. This gave us a statistical accuracy, in that particular count, of 1%. Where possible, particularly in the case of carbon-14, we count to a total greater than 10 000. Thus the overall accuracy of 2% is attainable.

**R. Glascock**: I admire Dr. Whitehead's faith in statistics, but I would like to ask him whether he actually finds that the replicate counts of 10 000 agree within the statistical limit predicted.

**J. K. Whitehead**: The answer is yes.

**N. H. Christensen** (Denmark): I might call Mr. Beale's attention to the fact

that Dr. Keston's original pipsyl method for the analysis of steroid hormones has been further developed by Dr. Bojesen, one of his pupils, so that at Copenhagen we are now able to determine, for example, andosterone in quantities down to  $10^{-5}$   $\mu$ mole, which is the same sensitivity as that of Mr. Beale's method on amino acids. I think, that several of his objections to the pipsyl methods are no longer valid. However, I would like to ask him whether anything in his experience would point to the possibility of making labelled dinitro derivates of steroid hormones with reproducible yields. If that were possible, the way would be open for applying the DNP method also for analyses of steroid hormones.

**D. Beale:** I am grateful for the information about Dr. Keston's work. This value of  $10^{-5}$  micromoles which he quotes is comparable with our own sensitivity value, which of course it should be in this type of derivative analysis. As I said before, it depends purely on the specific activity of the labelled reagent employed. As regards the use of the dinitrophenyl method for steroid hormones, this type of derivative analysis is of course applicable to the estimation of mixtures of any compound forming suitable derivatives which can be separated efficiently by paper chromatography. I should mention, however, that Dr. Tait and Mr. Ayres, colleagues of mine working at the Middlesex Hospital, have used the acetyl method with considerable success. They have not used the dinitrophenyl method because it has been developed only recently and the work we want to use it for has not even been started.

**B. Gordon** (United States of America): I would like to ask Mr. Beale whether, in his preparation of these labelled dinitrophenyl compounds, he made any kind of analytical test or established their radiochemical purity, as distinguished from their ordinary chemical purity? I do not believe that simple recrystallisation is enough to purify a compound radiochemically. I think that this would be a fairly important matter — considering that he is using a carbon-14 compound to monitor the loss of his tritium-labelled compound — because unless the same impurities and the same amount of impurities were present in both, his loss corrections using carbon-14 might possibly be in error when applied to the tritium derivative.

**D. Beale:** I agree that it is essential, in the separation of the labelled derivatives, to ensure that the compound isolated on the paper chromatogram is radiochemically pure, i. e. that no label contaminants should be present. As regards the preparation of the compounds — for instance, the tritiated fluorodinitrobenzene — could have been, and probably was, contaminated with the bromodinitrobenzene, but if it reacted with our amino acids, it would of course have the same specific activity as the fluorodinitrobenzene and therefore yield a labelled dinitrophenyl derivative of the amino acid having the same specific activity. The  $C^{14}$ -DNP-amino acids were checked by chromatography in two different systems. I therefore think that Mr. Gordon's point has been covered in our paper and that comparison of our results with those obtained by other methods (non-isotopic, derivative analysis, chromatographic) shows that the analytical side of our method is fairly sound.

**P. Springell** (Australia): Mr. Beale's recovery of DNP carbon-14 amino acids is very low. How does he account for this and does he consider this extensive destruction of DNP amino acids to be normal.

**D. Beale:** I am glad this question has been raised, because the recovery values are misleading. In the case of the estimation of the amino acids, they are not destruction values but values for losses occurring in manipulation procedures after reaction with the tritiating reagent. These losses depend on the chromatographic system and the system we employed originally, although their resolution was

reasonably good; tended to cause spreading of the spots. We are limited in the size of spot we can take by the nature of our apparatus which can hold a limited volume of carbon dioxide and water vapour. Thus, our recoveries are not breakdown factors but purely manipulation loss.

**E. A. Evans** (United Kingdom): What change in specific activity was observed in going from bromobenzene-tritium to the reagent 1-fluoro-2,4-dinitrobenzene T.

**D. Beale:** The actual yields in material that we obtained are shown in the paper. As regards the activity, two-fifths of our specific activity was lost due to the replacement of tritium by nitro groups. This is of course reflected in the value we obtained. However, I think that if a calculation were made by multiplying our specific activity of the reagent by our dilution factor and again by the inevitable loss of tritium through nitration, it would be found that our values for specific activities are very reasonable.

# ИЗМЕРЕНИЕ СПЕКТРОВ ТРИТОНОВ В ЯДЕРНЫХ РЕАКЦИЯХ

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Abstract — Résumé — Аннотация — Resumen

**Measuring the spectra of tritons in nuclear reactors.** A proposed method of measuring the energy and angular distributions of tritium nuclei formed in nuclear reactors is described. Around the target being bombarded by a beam of charged particles are arranged piles of foil, in which the escaping tritons are caught. After irradiation the tritium is separated from the foil and its activity measured by a Geiger counter. Characteristic features of the method are the complete absence of background from other charged particles and the possibility of simultaneously measuring the spectra at broad energy and angular intervals.

**Mesure des spectres des tritons durant les réactions nucléaires.** Les auteurs ont mis au point une méthode permettant de mesurer la distribution énergétique et angulaire des noyaux de tritium qui se forment durant les réactions nucléaires. Autour des cibles bombardées par un faisceau de particules chargées, on dispose des piles de feuilles destinées à capturer les tritons libérés. L'irradiation terminée, le tritium est séparé des feuilles et son activité est mesurée à l'aide d'un compteur Geiger. La méthode présente l'avantage de supprimer totalement le bruit de fond dû aux autres particules retenues et de rendre possible la mesure simultanée des spectres dans un grand intervalle énergétique et angulaire.

**Измерение спектров тритонов в ядерных реакциях.** Предложен и разработан метод измерения энергетических и угловых распределений ядер трития, образующихся в ядерных реакциях. Вокруг мишени, бомбардируемой пучком заряженных частиц, располагаются стопки фольг, в которых улавливаются вылетающие тритоны. После облучения тритий выделяется из фольг, и его активность измеряется гейгеровским счетчиком. Метод характеризуется полным отсутствием фона других заряженных частиц и возможность одновременного измерения спектров в широких энергетическом и угловом интервалах.

**Medición de los espectros de los tritones en las reacciones nucleares.** Los autores presentan un método para medir las distribuciones energéticas y angulares de los núcleos de tritio que se forman en las reacciones nucleares. Alrededor del blanco bombardeado con un haz de partículas cargadas se coloca una pila de láminas metálicas que capturan los tritones emitidos. Después de la irradiación, el tritio se separa de las láminas y su actividad se mide con un contador Geiger. El método se caracteriza por la total ausencia de actividad de fondo atribuible a otras partículas cargadas y por la posibilidad de medir simultáneamente los espectros en amplios intervalos energéticos y angulares.

## 1. Введение

Экспериментальное изучение реакций с образованием слабо связанных частиц — дейтонов, тритонов и ядер  $\text{He}^3$  — представляет известные трудности, связанные с тем, что из-за малой энергии связи образующихся частиц эти реакции оказываются, как правило, сильно эндотерми-

ческими. Поэтому при использовании обычных детекторов (различных счетчиков, фотопластинок) образующиеся сравнительно медленные дейтроны, тритоны и ядра  $\text{He}^3$  приходится наблюдать на фоне более энергичных частиц, который обычно значительно превышает эффект. Различные способы дискриминации частиц по массе практически позволяют исследовать лишь жесткую часть спектра, соответствующую небольшим энергиям возбуждения остаточных ядер.

Существует, однако, возможность исследовать один из видов указанных реакций, а именно реакции с образованием тритонов, в условиях, совершенно свободных от фона других частиц. При этом ширина исследуемого интервала энергий возбуждения остаточных ядер определяется лишь энергией падающих частиц. Эта возможность, связанная с радиоактивностью трития, была использована в описанном ниже методе исследования ядерных реакций под действием заряженных частиц, ускоренных на циклотроне Института атомной энергии [1].

Сущность метода состоит в следующем. Пусть пучок тритонов различной энергии падает нормально на стопку фольг, толщина которой превышает пробег тритонов максимальной энергии. В результате ионизационных потерь тритоны тормозятся, и каждый тритон останавливается в той или иной фольге, в зависимости от своей первоначальной энергии. Измеряя активность трития, накопленного в каждой отдельной фольге, можно получить распределение тритонов по пробегам и, следовательно, по энергии. Если тритоны образуются в некоторой мишени в результате ядерной реакции, то установив стопки фольг под различными углами к пучку падающих частиц, можно получить распределение тритонов по углам и по энергии.

Очевидно, что данный метод является совершенно бесфоновым, так как все другие заряженные частицы, образующиеся в ядерных реакциях (протоны, дейтроны, ядра  $\text{He}^3$  и  $\text{He}^4$ ), стабильны. Что касается более тяжелых радиоактивных ядер отдачи, то их пробег во много раз меньше пробега тритонов и они практически несущественны.

## 2. Устройство для сбора трития

Для измерения спектров и угловых распределений тритонов применялась вакуумная камера (рис. 1), в центре которой помещалась мишень, а вокруг нее — фольги для улавливания тритонов. Пучок падающих частиц, после прохождения прямоугольной диафрагмы (обычно размером  $10 \times 12$  мм) попадал на мишень и затем в цилиндр Фарадея, соединенный с интегратором тока. Все детали камеры, на которые мог попадать пучок (диафрагмы, стенки и заглушка цилиндра Фарадея, стенки тракта пучка) были изготовлены из графита, чтобы после облучения не возникало долгоживущих активностей. Мишень, представлявшая собой либо фольгу, либо тонкий слой окисла или соли, нанесенный на подложку путем напыления или осаждения, закреплялась в рамочке, которая могла устанавливаться по отношению к пучку под углом, кратным  $22,5^\circ$ . Для работы с мишенями, окисляющимися на воздухе (например, из металлического лития) были изготовлены специальные камеры с вакуумной заслонкой, поз-

волявшие без нарушения вакуума готовить мишень путем нанывления, переносить ее и устанавливать в устройство для облучения.

Для улавливания тритонов применялись алюминиевые фольги. Алюминий весьма удобен в качестве материала для собирающих фольг, так как пробег тритонов в нем достаточно велик и можно получить

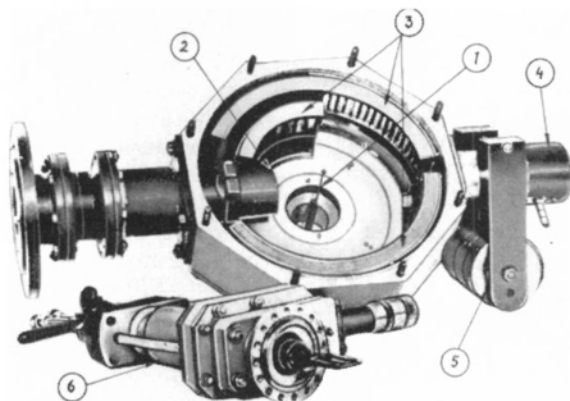


Рис. 1

Вакуумная камера для облучений и сбора трития: 1 — мишень; 2 — входной коллиматор; 3 — кассеты с собирающими фольгами; 4 — цилиндр Фарадея; 5 — магнит, препятствующий вылету вторичных электронов; 6 — камера для мишеней, окисляющихся на воздухе.

хорошее разрешение по энергии, используя сравнительно толстые фольги, выпускаемые промышленностью. Обычно применялись фольги толщиной  $2,15 \text{ мг/см}^2$  ( $8 \mu$ ). Фольги укладывались в виде стопок лент в кассеты, которые помещались по кругу на расстоянии 150 мм или 100 мм от центра мишени. Тритоны, вылетающие из мишени, попадали на фольги через широкое окно в кассетах, имевшее высоту 40 мм и разделенное для фиксирования угла вылета тритонов перемычками шириной 3 мм. Перемычки располагались через  $4^\circ$  на радиусе 150 мм и  $8^\circ$  на радиусе 100 мм. Угловой интервал между перемычками составлял  $2,8^\circ$  и  $6,4^\circ$  соответственно. Минимальный угол регистрации тритонов был  $6^\circ$ , максимальный —  $150^\circ$ . После облучения кассеты вынимались из камеры, и фольги разрезались в местах, закрытых во время облучения перемычками.

### 3. Выделение трития

Так как  $\beta$ -частицы, образующиеся при распаде трития, очень мягкие (граница  $\beta$ -спектра 18 кэв, что соответствует пробегу электронов  $\sim 0,5 \text{ мг/см}^2$ ), то для измерения активности трития его необходимо выделить из фольги и затем ввести внутрь счетчика.

Выделение трития может быть осуществлено либо нагреванием фольги, либо ее растворением. Наиболее удобным способом, позволяющим быстро выделять тритий из большого числа образцов, является

нагревание. При этом соединения трития с атомами фольги, образовавшиеся после остановки тритонов, разлагаются, и тритий выделяется в результате диффузии, скорость которой экспоненциально растет с температурой. Либби и др. отмечали [2], что практически полное выделение трития из бериллия и алюминия происходит при температуре 900° С.

Нами были проведены опыты по выделению трития нагреванием из различных металлов (Al, Mg, Cu, Zn, Sn, Bi). На пластинки из этих металлов был напылен тонкий слой  $LiF$ . Пластинки одновременно облучались потоком тепловых нейтронов, и образующиеся в результате реакции  $Li^6 (n, t) He^4$  тритоны накапливались в слое металла. Из всех облученных образцов при прогревании их при температуре 900° в течение 10—15 мин. выделялись одинаковые количества трития, совпадавшие с расчетными.

Выделение трития из собирающих алюминиевых фольг производилось следующим образом. Каждая фольга помещалась в кварцевую ампулу диаметром 6—10 мм и высотой 100—120 мм, имевшую стеклянный кран, присоединенный к ампуле при помощи шлифа. Вместе с фольгой в ампулу помещался предварительно хорошо обезгаженный кусочек графита, служивший тиглем. Ампула наполнялась до давления 80 мм Hg водородом, выполнявшим роль носителя. После этого она устанавливалась в индукторе высокочастотной печи (мощность печи 2 киловатта, частота генератора 8 мГц) и подогревалась при температуре 1200° в течение 6 мин. После остывания ампула соединялась со счетчиком резиновым шлангом длиной около 10 см, а активированный тритием водород напускался в счетчик. Для ускорения работы производился нагрев одновременно восьми ампул. С этой целью был изготовлен специальный индуктор из восьми катушек.

Повторное выделение трития давало не свыше 1—2% первоначальной активности и поэтому, как правило, не производилось. Потери трития в крановой замазке, на стенках ампул и в графитовых тиглях были весьма малы.

Диффузии трития из облученных фольг при их хранении не было обнаружено.

#### 4. Измерение активности трития

Для измерения активности трития использовался гейгеровский счетчик [2—4]. Счетчик наполнялся смесью метилала с аргоном (15—20% метилала при полном давлении 80—100 мм Hg). Давление водорода в счетчике было не свыше 3—5 мм Hg за счет того, что объем ампулы и соединительного шланга был примерно в 30 раз меньше объема счетчика. Плато счетчика при давлении водорода до 15 мм Hg имело длину свыше 150 в и наклон менее 5%.

Установка содержала восемь одинаковых счетчиков. Общий вид установки приведен на рис. 2. Откачка счетчика и всей системы наполнения проводилась форвакуумным насосом. Активированный тритием водород напускался из ампул в откачанные счетчики. После этого в счетчики напускалась рабочая смесь, причем давление смеси в системе наполнения все время превышало ее давление в счетчике.



Счетчики были изготовлены из медной трубки внутренним диаметром 25 мм. Длина нити счетчиков составляла 268 мм. Длина неэффективного участка нити, вызванного концевыми эффектами, была измерена в опытах с тремя счетчиками различной длины и оказалась равной 14 мм.

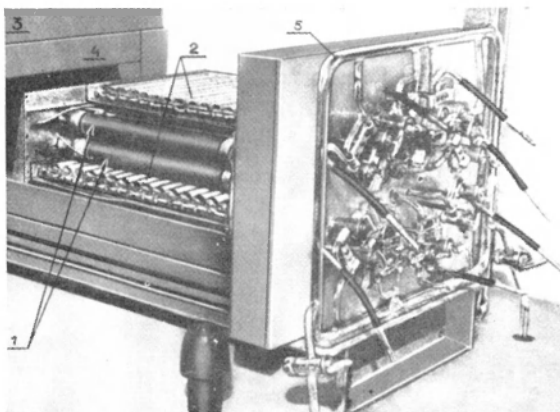


Рис. 2.

Общий вид измерительной установки: 1 — счетчики для измерения активности трития; 2 — счетчики антисовпадений; 3 — свинцовая защита; 4 — железная защита; 5 — система наполнения.

Поправка на краевой эффект для  $\beta$ -частиц трития пренебрежимо мала [5]. Отношение эффективного объема счетчика к полному объему счетчика, соединительного шланга и ампулы было равно 0,60.

Для уменьшения фона счетчики были защищены слоями железа (внутренний слой) и свинца толщиной по 5 см. Кроме того, сверху и снизу рабочих счетчиков находились ковры из гейгеровских счетчиков, включенных с каждым из рабочих счетчиков на антисовпадения. При этом фон был все же довольно велик (30 имп/мин), что объясняется, по-видимому, большими радиоактивными загрязнениями конструктивных материалов.

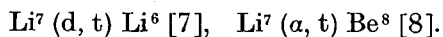
При измерении активностей до нескольких тысяч импульсов в минуту счетчик не обнаруживал какого-либо остаточного фона после откачки в течение нескольких минут и нескольких напусков воздуха. Отсутствие «памяти» было установлено не только для используемого счетчика с гладким медным катодом, но и для изготавливаемых промышленностью счетчиков с катодом из порошкообразной меди и для счетчиков с катодом из нержавеющей стали.

Колебания чувствительности счетчиков при перенаполнениях проверялись с кобальтовым источником и не превышали 2—3%.

## 5. Результаты

Распределение тритонов по пробегам пересчитывалось в распределение по энергии при помощи кривой пробег-энергия для тритонов в Al, полученной из кривой пробег-энергия Смита [6] для протонов.

Для иллюстрации возможностей метода на рис. 3—4 приведены спектры тритонов, измеренные в реакциях



В случае реакции  $(d, t)$  спектр обнаруживает три острых пика, соответствующих первым трем состояниям ядра  $\text{Li}^6$ . Ширина максимумов

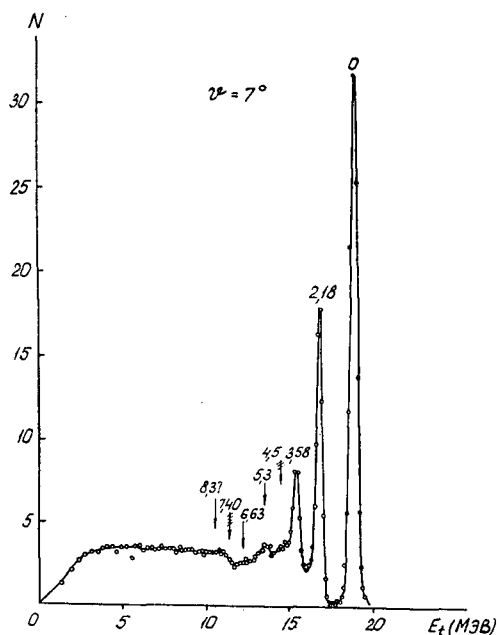


Рис. 3.

Спектр тритонов в реакции  $\text{Li}^7 (d, t) \text{Li}^6$  под углом  $7^\circ$ . Энергия дейтронов — 20 Мэв.

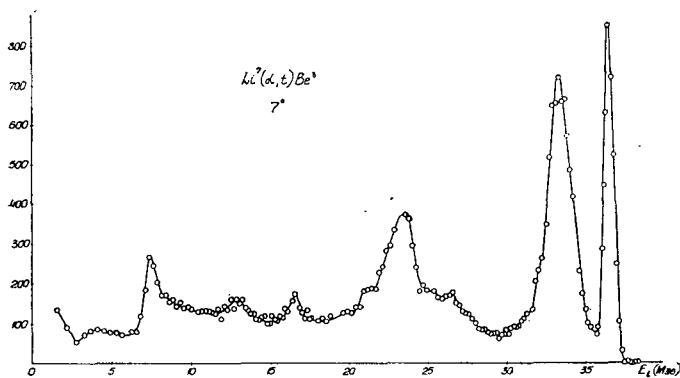


Рис. 4.

Спектр тритонов в реакции  $\text{Li}^7 (\alpha, t) \text{Be}^8$  под углом  $7^\circ$ . Энергия  $\alpha$  — частиц — 40 Мэв.

является аппаратурной (толщина мишени  $3 \text{ мг/см}^2$ ). Спектр, полученный в реакции  $\text{Li}^7(\alpha, t)\text{Be}^8$ , демонстрирует возможность измерений в весьма широком диапазоне энергий.

Разрешающая способность по энергии определяется следующими факторами:

1. Степень монохроматичности пучка первичных частиц.
2. Толщина мишени.
3. Толщина собирающих фольг.
4. Ширина углового интервала, захватываемого собирающими фольгами.
5. Стрэглинг тритонов в собирающих фольгах.

Эти факторы по разному зависят от энергии тритонов. Энергетическая толщина мишени и собирающих фольг убывает с энергией тритонов (как  $dE/dx$ ), в то время как абсолютная величина стрэглинга растет. Суммарная аппаратурная ширина, как видно из рис. 5, вначале

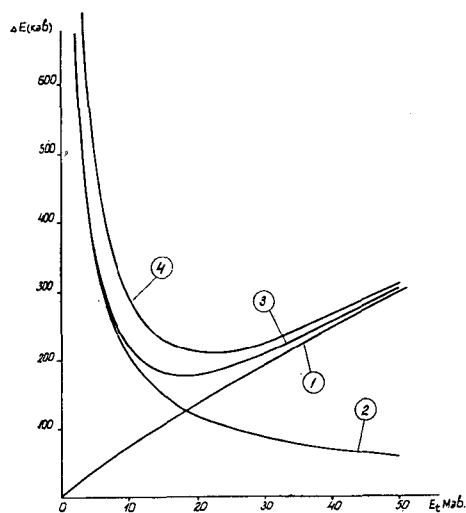


Рис. 5.

Зависимость аппаратурной ширины от энергии тритонов: 1 — стрэглинг; 2 — разброс в мишени и фольге общей толщиной  $3,6 \text{ мг/см}^2$ ; 3 — аппаратурная ширина при толщине  $3,6 \text{ мг/см}^2$ ; 4 — то же при  $5 \text{ мг/см}^2$ . Разброс энергий в пучке и в угловом интервале принят равным нулю.

убывает с энергией тритонов, а затем начинает медленно расти. Положение минимума зависит от толщины мишени и собирающих фольг.

Описываемый метод по энергетической разрешающей способности не уступает другим методам спектрометрии заряженных частиц, за исключением магнитного анализа.

Угловое разрешение, получаемое в данном методе, не имеет каких-либо специфических особенностей по сравнению с другими методами регистрации частиц. Практически оно ограничивается требованием

собрать в фольгах тритий в количестве, необходимом для надежного его измерения.

Основным недостатком метода является его низкая чувствительность, связанная с тем, что период полураспада трития весьма велик ( $T^{1/2} = 12,26$  года [9],  $\lambda = 1,075 \cdot 10^{-7}$  мин). Чтобы скорость счета в счетчике составляла 10 имп/мин., необходимо собрать в фольге  $\sim 10^8$  атомов трития. Поэтому измерение спектров тритонов при хорошем энергетическом и угловом разрешении возможно лишь для реакций, сечения которых больше 0,1—0,2 мб/стер. (при облучении  $\sim 100$  мк. час). Этот предел может быть значительно понижен при измерении спектров в широких угловых интервалах, что возможно, если энергия вылетающих тритонов мало зависит от угла.

Ошибка относительных измерений спектров тритонов складывается из разброса средних толщин фольг ( $\pm 1\%$  для используемых фольг), неполного выделения и потерь трития ( $\pm 1,5\%$ ), изменения эффективности счетчика при перенаполнениях ( $\pm 1,5\%$ ) и статистической ошибки. При определении абсолютной величины сечения добавляются еще ошибка в абсолютной калибровке счетчика ( $\pm 5\%$ ), а также общие для всех методов изучения ядерных реакций ошибки в измерении потока падающих частиц, толщины мишени и телесного угла.

## 6. Измерение полных сечений

Описанным методом можно измерять также полные сечения образования трития. Выделение трития и измерение его активности производится в этом случае так же, как и при измерении спектров. Различие состоит лишь в способах сбора трития.

Измерение активности трития применялось ранее для измерения кривых возбуждения реакций  $\text{Be}^9(d, t)$  [2, 10],  $\text{Li}^6(d, t)$  и  $\text{Li}^7(d, t)$  [11]. Нами этот метод был использован для измерения кривой возбуждения реакции  $\text{Li}^7(p, t)$  [12].

Для сбора трития применялось устройство, изображенное на рис. 6. Мишенями служили слои фтористого лития толщиной 10—15 мг/см<sup>2</sup>, нанесенные на алюминиевые подложки. Толщина подложек превышала пробег тритонов максимальной энергии. Для уменьшения энергии падающих протонов перед мишенями помещались стопки алюминиевых фольг. Каждая мишень помещалась на дно стакана, на боковой поверхности которого имелась свернутая в цилиндр оловянная фольга. Тритоны, летящие в переднюю полусферу, останавливались в подложке, а летящие в заднюю полусферу — в стопке тормозящих фольг и в боковой фольге. Телесный угол отверстия в стакане, через который проходил пучок первичных частиц, составлял немногим более 1% от полного. Стаканы крепились на общей несущей пластине, изолированной от диафрагмы и соединенной с интегратором тока. Всего имелось 15 стаканов, каждый из которых мог поочередно устанавливаться под пучком. Управление перемещением стаканов осуществлялось дистанционно. После облучения тритий выделялся одновременно из мишени с подложкой тормозящих фольг и соответствующей боковой фольги.

При использовании этого метода для измерения кривых возбуждения необходимо использовать подложки из веществ, у которых сечение

образования трития мало по сравнению с исследуемым элементом. Кроме того надо иметь в виду, что в некоторых случаях в облученном веществе наряду с тритием могут образовываться другие радиоактивные

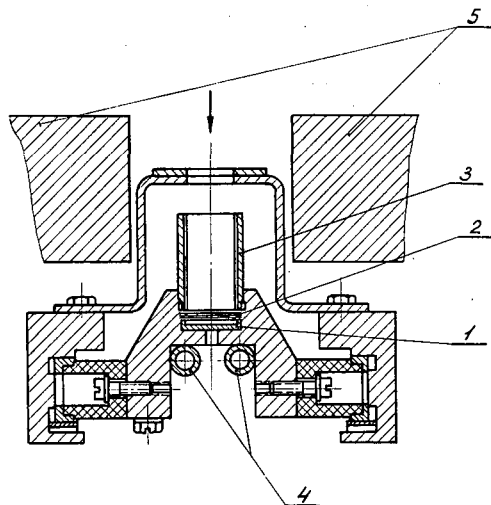


Рис. 6.

Устройство для измерения полных сечений: 1 — мишень; 2 — фолги для уменьшения энергии падающих частиц; 3 — боковая фольга; 4 — трубки охлаждения; 5 — магнит, препятствующий вылету вторичных электронов.

газы. Поэтому необходимо отделять тритий от посторонних радиоактивных газов, например, используя палладиевый фильтр [13].

## 7. Заключение

Описанный метод оказался весьма полезным для исследования реакций с образованием тритонов. С его помощью было проведено детальное исследование реакций  $(d, t)$  на многих ядрах [7, 14—18], а также реакций  $(\alpha, t)$  [8] и  $(p, t)$  [12]. Были получены весьма интересные данные как об особенностях этих реакций, так и о свойствах исследованных ядер, которые трудно получить при использовании других методов.

Мы глубоко благодарны Н. А. ВЛАСОВУ, С. П. КАЛИНИНУ за помощь и постоянный интерес к работе и А. Г. ОБРАЗЦОВУ за участие в измерениях.

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### DISCUSSION XIII

W. F. Libby (United States of America): My compliments to the speaker on the beautiful research. Could he describe the method by which the tritium is extracted from the aluminium catcher foils? Were the foils melted or were they dissolved in alkaline solution?

A. Ogloblin (Union of Soviet Socialist Republics): The foils were melted at about 1200 °C.

C

DETECTION AND COUNTING OF TRITIUM

(Sessions III—IV)





# LIQUID SCINTILLATION DETECTION OF TRITIUM AND OTHER RADIOISOTOPES IN INSOLUBLE OR QUENCHING ORGANIC SAMPLES

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Abstract — Résumé — Аннотация — Resumen

**Liquid scintillation detection of tritium and other radioisotopes in insoluble or quenching organic samples.** To facilitate a study of the  $H^1/H^3$  isotope effect in the reduction of organic compounds, it has been necessary to develop procedures to overcome the two major limitations of the most convenient general method of radioassaying organic material, liquid scintillation counting. These limitations, which are scintillation-quenching by many organic samples and limited solubility of others, are particularly common with material of biological significance. The procedures developed involve combustion of the sample wrapped in filter paper in an oxygen-filled flask, formation of a solution of the combustion products in a suitable solvent added to the flask before combustion, and scintillation-counting of the solution. Advantages of the developed procedures, in addition to overcoming the indicated limitations, include efficacy with samples with a great range of activity (some as low as  $1 \mu\text{C}/\text{mole}$ ), good precision (as great as any other general method of radio-assaying  $H^3$ ), and applicability to other soft beta emitters ( $C^{14}$  and  $S^{35}$ ). With a scintillation spectrometer and the techniques developed, samples triply labelled with  $H^3$ ,  $C^{14}$  and  $S^{35}$  can be differentially radio assayed.

Details of the solvent systems and techniques developed are reported. Analytical results are reported for such quenching material as 2,4-dinitrophenyl-hydrazones dyes and for such insoluble materials as proteins and carbohydrates. Application of the techniques to evaluation of  $H^1/H^3$  isotope effects in certain reduction reactions are discussed.

**Détection par compteur à scintillations à liquides du tritium et des autres radioéléments contenus dans des échantillons organiques insolubles ou coupeurs.** Pour faciliter l'étude de l'effet isotopique  $H^1/H^3$  dans la réduction des composés organiques, il a fallu mettre au point des procédés permettant d'élargir le champ d'application de la méthode générale la plus pratique de radioanalyse des matières organiques, savoir l'analyse au moyen d'un compteur à scintillations à liquides. En effet, ce champ d'application est limité pour deux raisons: beaucoup d'échantillons organiques provoquent le coupage; d'autres échantillons sont peu solubles. Ces limitations sont particulièrement fréquentes dans le cas des substances importantes du point de vue biologique. Le procédé mis au point par les auteurs comporte la combustion de l'échantillon enveloppé de papier filtre, dans un ballon rempli d'oxygène; la dissolution des produits de combustion dans un solvant approprié ajouté au ballon avant la combustion; enfin, le comptage de la solution. Parmi les avantages de ce procédé, on relèvera — outre le fait qu'il permet d'élargir le champ d'application de la méthode en supprimant les limitations mentionnées plus haut — son efficacité pour des échantillons ayant des activités extrêmement diverses (dans certains cas, elles ne dépassent pas  $1 \mu\text{C}$  par mole), son excellente précision (aussi grande que celle de toute autre méthode générale de radioanalyse du tritium) et la possibilité de l'appliquer à d'autres émetteurs bêta mous ( $C^{14}$  et  $S^{35}$ ). Avec un spectromètre à scintillations et le procédé mis au point par les auteurs, des échantillons marqués par trois indicateurs (tritium, carbone-14 et soufre-35) peuvent faire l'objet d'une radioanalyse différentielle.

Les auteurs donnent des détails sur les solvants utilisés et les techniques mises au point, et indiquent les résultats de l'analyse pour des matières provoquant le coupage telles que les dinitro-2,4, phénylhydrazones et les colorants au thiazole, ainsi que pour des matières insolubles telles que les protéines et les hydrates de carbone. Ils rendent compte de l'application du procédé à l'évaluation des effets isotopiques  $H^1/H^3$  dans certaines réactions de réduction.

**Обнаружение трития методом жидкостной сцинтилляции в нерастворимых или способных гасить излучение органических образцах.** Чтобы облегчить изучение влияния изотопа  $H^1/H^3$  на восстановление органических соединений необходимо было разработать процедуры для преодоления двух основных ограничений в наиболее удобном общем методе измерения радиоактивности органических веществ посредством жидкостного сцинтиллятора. Эти ограничения, которыми являются сцинтилляционное гашение многими органическими образцами и ограниченная растворимость других, присущи также биологическим веществам. Разработанные процедуры включают в себя окисление обернутого в фильтровальную бумагу образца в колбе, наполненной кислородом, образование раствора окисленных продуктов в соответствующем растворителе, добавленном в колбу перед окислением, и сцинтилляционный счет раствора. Преимущества разработанных процедур для преодоления указанных ограничений включают: качество операции с образцами большого диапазона активности (некоторые с такой низкой активностью как  $1 \mu\text{с}/\text{mole}$ ), большую точность (такую же как при любом другом общем методе измерения радиоактивности  $H^3$ ), и применимость к другим мягким бета-излучателям ( $C^{14}$  и  $K^{35}$ ). С помощью сцинтилляционного спектрометра и разработанных процедур может быть раздельно измерена радиоактивность образцов меченных трижды  $H^3$ ,  $C^{14}$  и  $K^{35}$ .

Детали, касающиеся систем растворителя и разработанных методов, будут изложены в докладе, кроме того в нем будет дана рабочая характеристика нового, относительно недорогого одноканального сцинтилляционного спектрометра. Будут изложены аналитические результаты, касающиеся такого гасящего излучение материала, как 2,4-динитро-фенилгидрозоны и тиазолиды, а также таких нерастворимых материалов, как протеины и углеводы. Будет обсуждено применение методов к оценке изотопного эффекта  $H^1/H^3$  в определенных реакциях восстановления.

**Detección del tritio y otros radioisótopos por centelleo líquido en muestras orgánicas insolubles o que provocan extinción.** Para facilitar el estudio del efecto isotópico  $H^1/H^3$  en la reducción de compuestos orgánicos, ha sido preciso idear procedimientos a fin de vencer los dos inconvenientes principales que presenta el método de radioanálisis general más apropiado para las sustancias orgánicas, a saber, el recuento por centelleos de líquidos. Estos inconvenientes, que son la extinción del centelleo producida por muchas muestras orgánicas y la escasa solubilidad de otras, son particularmente frecuentes en las sustancias de importancia biológica. El procedimiento ideado por los autores consiste en lo siguiente: combustión de la muestra, envuelta en papel de filtro, en un matraz lleno de oxígeno; disolución de los productos de combustión en un disolvente adecuado que se introduce en el matraz antes de la combustión, y recuento por centelleo de la actividad de la solución. Además de superar los inconvenientes mencionados, este procedimiento posee otras ventajas: eficacia con muestras de actividades muy diversas (algunas, tan baja como  $1 \mu\text{с}/\text{M}$ ), precisión (tan elevada como la de cualquier otro método general de radioanálisis del  $^3\text{H}$ ) y posibilidad de aplicarlo a otros emisores beta blandos ( $^{14}\text{C}$  y  $^{35}\text{S}$ ). Con un espectrómetro de centelleo y merced al procedimiento ideado, es posible efectuar un radioanálisis diferencial de muestras marcadas con tres indicadores ( $^3\text{H}$ ,  $^{14}\text{C}$  y  $^{35}\text{S}$ ).

Los autores describen con detalle las técnicas y los sistemas de disolventes utilizados. Asimismo, exponen los resultados obtenidos en el análisis de sustancias que provocan extinción, como 2,4-dinitrofenilhidrazonas y colorantes de tiazol, y de sustancias insolubles, como proteínas e hidratos de carbono. Estudian la aplicación de estas técnicas al análisis de los efectos isotópicos  $H^1/H^3$  en ciertas reacciones de reducción.

## Introduction

Although direct liquid scintillation counting of radioactive organic compounds has proved to be the most convenient general method for their radioassay, limited

solubility of much organic material and scintillation-quenching by other organic compounds constitute two important limitations of this method. The techniques previously reported for overcoming limitations, such as combustion of the samples before assay and/or counting of two-phase system [1], so decrease the convenience or efficiency of scintillation-counting that other counting methods, usually ion-current methods [2], are preferable for analysis of insoluble or strongly-quenching organic material. These limitations frequently are particularly severe with samples of biological significance. Reported here is the technique which we have begun to use to overcome these limitations and which we have found to be a convenient and efficient scintillation-counting technique for each of the three  $\beta$ -emitters most commonly found in organic material, tritium, carbon-14 and sulphur-35. The technique involves combustion of the sample wrapped in filter paper and in an oxygen-filled flask, formation of a solution of the combustion products in a solvent added to the flask before combustion and scintillation-counting of an aliquot of the solution.

### Experimental

There follow two procedures used for preparing samples for assay by scintillation counting. The detector portion of the liquid scintillation counter used, the Baird Atomic Model 745, was kept in a freezer chest at  $-18^{\circ}$ . The "toluene counting solution" was prepared by dissolution of 4 g of 2,5-diphenyloxazole, "PPO", and 0.05 g of 2,2-p-phenylene-bis-(5-phenyloxazole), "POPOP", in one liter of toluene. The "methanol counting solution" was prepared by mixing of 350 ml of toluene counting solution with 150 ml of methanol. The "dimethylformamide counting solution" was prepared by dissolution of 1.5 g of PPO and 0.08 g of POPOP in a mixture of 100 ml of dimethylformamide and 200 ml of anisole. Procedure One was used for the assay of samples whose activities were in the range of millicuries per mole. Procedure Two was used for samples with a lower molar radioactivity. In both procedures, after the final solution was prepared for counting in a Wheaton glass vial, the vial was allowed to stand in the detector in the freezer chest for 30 min or until it showed an essentially constant counting rate before it was counted. Each observed counting rate was corrected for background and was converted to radioactivity units by comparison with the counting rate of 0.1 ml of an appropriate internal standard added to the vial. The internal standard used for tritium was toluene-4- $t$  in toluene. For carbon-14 and sulphur-35 a solution of benzoic acid-7- $C^{14}$  in anisole was employed.

The general technique of combustion of organic samples in a flask of oxygen has been previously described in detail [3].

#### PROCEDURE ONE

The sample, 2—15 mg, is prepared by being wrapped in a piece of filter paper (Whatman No. 42), 50—100 mg, so that a small paper tab extends from the packet. The packet is clamped in a coil of platinum wire sealed in a glass rod attached to the stopper of a 500-ml, heavy-wall Erlenmeyer flask. The flask is flushed with oxygen, and into it is pipetted 10 ml of either water (for tritium assays), 0.5% aqueous hydrogen peroxide (for sulphur assays) or 10% aqueous tetramethylammonium hydroxide (for carbon-14 assays). The extended tab of the packet is ignited and the stopper to which it is attached is fitted in the flask. After combustion is complete, the flask is rotated so as to rinse thoroughly all interior surfaces.

The aqueous solution is allowed to drain to one side of the flask bottom and an 0.1 or 0.2 ml aliquot of the aqueous solution is pipetted into either 15 ml of a methanol counting solution (for tritium assays), 15 ml of a dimethylformamide counting solution (for sulphur-35 assays) or 1 ml of methanol plus 15 ml of a dimethylformamide counting solution (for carbon-14 assays).

#### PROCEDURE TWO

The sample is prepared as described above, but it is inserted into a combustion flask which has a 15 ml test tube side arm sealed at a right angle to the flask just below its neck. The flask is clamped in a horizontal position with the side arm extending down into a Dewar flask of crushed dry ice. Five milliliters of a methanolic absorbing medium are pipetted into the cooled side arm of the flask, which is clamped behind a protective shield and flushed with oxygen just before the ignition packet is inserted into it. Absolute methanol is used for tritium analyses, three to four drops each of concentrated sulphuric acid and 30% aqueous hydrogen peroxide are added to the methanol for sulphur-35 analyses, and 10% benzyltrimethylammonium hydroxide in methanol is used for carbon-14 analyses. After combustion is complete, the flask is unclamped and inverted so that the methanol is poured out of the side arm over the interior surfaces. A 1 to 3 ml aliquot of the methanol solution is added to 15 ml of either toluene or methanol counting solution (for tritium or sulphur-35 assays) or dimethylformamide counting solution (for carbon-14 assays).

After either procedure, in calculating the fraction of the sample's activity taken in any aliquot, the volume of the absorbent originally added to the combustion flask should be increased by 0.05 ml to correct for water produced in the combustion.

Considerable modifications of the details of the above procedures have been successfully made in assays of tritium or carbon-14-labelled benzoic acid. For example, diethylamine (absolute or in methanol or in water) makes an inexpensive satisfactory absorbent of the combustion products. Further, the quantity of absorbent added to the combustion flask and the size of aliquot finally taken can be considerably varied, if necessary, so that at least 90% of the sample's activity can be taken in the aliquot.

#### Results and Discussion

Reproducibility and precision of the above techniques were determined by repeated analyses of radioactive benzoic acid. Ten analyses of tritium-labelled benzoic acid of an activity of 57.0 mc/mole showed an average value found of 57.1 mc/mole with a standard deviation of 0.4 mc/mole. Carbon-14-labelled acid of 11.07 mc/mole showed an average found value of 11.01 mc/mole with a standard deviation of 0.03 mc/mole. Analytical data for a number of additional compounds are shown in Table I. As an example of a compound which quenches too strongly to be counted directly, the 2,4-dinitrophenylhydrazone of tritium-labelled benzaldehyde, 27.3 mc/mole, was assayed and found to have  $26.9 \pm 0.3$  mc/mole. As samples of compounds insoluble in conventional liquid scintillation solvents, tritium-labelled leucine and glucose and sulphur-35-labelled cystine assays are shown in Table I.

In addition to overcoming the noted solubility and quenching limitations of liquid scintillation counting, the technique reported here has certain other advantages. For samples containing only carbon, hydrogen and oxygen, assaying can be carried out without recourse to an internal standard to give results of moderate accuracy, to

within about 5%. This is possible because the make-up of the final liquid scintillation solution is the same for each sample, regardless of the chemical structure of the original sample. Further, it is possible to assay sulphur-35 in the presence of carbon-14 by boiling of the solution in the flask after combustion of a sulphur compound. The sulphur, present after combustion as sulphuric acid, is retained long after the carbon dioxide is expelled.

TABLE I

**RESULTS FROM RADIOASSAY OF LABELLED ORGANIC SAMPLES COMBUSTED AND THEN COUNTED BY SCINTILLATION TECHNIQUE**

Compound assayed	Isotopic label	Millicuries per Mole	
		Present *	Found **
Glucose	1-H <sup>3</sup>	43.3	43.3 ± 0.1
Glucose	6-H <sup>3</sup>	46.1	46.1 ± 0.2
Leucine	2-H <sup>3</sup>	0.0702	0.0697 ± 0.0009
Benzaldehyde 2,4-dinitro-phenylhydrazone	7-H <sup>3</sup>	28.1	28.5 ± 0.2
Thiophene-2-carboxylic acid	5-H <sup>3</sup>	0.0059	0.0059 ± 0.0001
Benzoic Acid	4-H <sup>3</sup>	57.0	57.1 ± 0.4
Benzoic Acid	4-H <sup>3</sup>	0.578	0.58 ± 0.2
Benzoic Acid	7-C <sup>14</sup>	11.07	11.01 ± 0.03
Polystyrene	C <sup>14</sup>	0.720	0.720 ± 0.0002
1,2-Diphenylethyleneglycol	1-C <sup>14</sup>	2.35	2.37 ± 0.02
Ethyl Triphenylacetate	1-C <sup>14</sup>	7.62	7.67 ± 0.04
Thiourea	S <sup>35</sup>	5.36	5.35
Cystine	S <sup>35</sup>	2.43	2.45 ± 0.05
Cystine	S <sup>35</sup>	0.143	0.147 ± 0.002
Cystine***	S <sup>35</sup>	0.234	0.242 ± 0.006

\* The activities present as H<sup>3</sup> and C<sup>14</sup> were determined by appropriate ion chamber counting techniques and/or direct scintillation counting. The activities present as S<sup>35</sup> were redetermined periodically and extrapolated to give the values present at the time the reported analyses were made.

\*\* The found values reported are averaged from duplicate or triplicate runs in most cases.

\*\*\* Some samples of cystine were combusted in the presence of excess C<sup>14</sup>-benzoic acid.

Table I shows some values determined for sulphur-35-labelled cystine (about 0.2 mc/mole) determined by combustion along with an equal weight of carbon-14-labelled benzoic acid (about 60 mc/mole). Despite the original presence of the large excess of activity due to carbon-14, the correct value for sulphur-35 was found. Since a scintillation spectrometer will differentially count either carbon-14 or sulphur-35 in the presence of tritium, the techniques reported here now allow one to radioassay each of the isotopes in samples triply labelled with tritium, carbon-14 and sulphur-35.

The chief limitation on the techniques reported here will probably be that of limited sample size suitable for burning in an flask of oxygen. Samples as large as 100 mg have been reported to have been burned in a 500 ml flask. With samples this large no difficulty is anticipated for analysis of tritium or sulphur-35. However, the quantity of carbonates produced with samples this large would present some solubility difficulties for the analysis of carbon-14.

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## DISCUSSION XIV

**J. Varshavsky** (Union of Soviet Socialist Republics): The methods of preparing samples for analysis, as described in the paper of Prof. Eastham, involve procedures which are well known and widely used in laboratories. These methods are based on common organic analytical procedures which have been in use for many years. What new principle is he introducing?

**J. Eastham** (United States of America): I did not know that there are established procedures in which ammonia is used to exchange hydrogen for tritium and then counted in an ion chamber or in which samples simultaneously labelled with tritium, carbon-14 and sulphur-35 can be assayed for each isotope.

**F. Kalberer** (Switzerland): I can report that we have development a very similar combustion technique at the Sandoz Laboratory in Basel and will publish our results in an early issue of *Helvetica Chimica Acta*.

**J. Eastham**: The comment of Mr. Kalberer shows that I am not alone in my ignorance of the procedures mentioned by Dr. Varshavsky. It was at the Sandoz Laboratory that Schöniger developed the combustion in a flask.

**N. I. Berlin** (United States of America): I should like to ask Prof. Eastham how much material he can combust in the Schöniger combustion flask.

**J. Eastham**: This question touches on one of the main limitations of the technique. It is a matter to which I have referred in the paper. We have combusted samples of up to 20–25 mg and have satisfactorily analysed organic material containing as little as 1 or 2  $\mu\text{C}/\text{mole}$  by this technique (I have read that up to 500 mg can be combusted in a flask, but I think that a shield would be required in this case).

**E. A. Evans** (United Kingdom): I should like to ask Prof. Eastham what he does about combusting volatile material in a Schöniger flask, and what method he uses to pack the samples.

**J. Eastham**: I have not actually counted any volatile compounds. Non-volatile liquids can be adsorbed directly on the paper combusted. I am informed that, for ordinary Schöniger combustion, volatile liquids can be weighed into gelatin capsules or into open-ended capillary tubes, which are then wrapped in the paper and combusted.

**P. Springell** (Australia): I would like to ask Prof. Eastham how many samples a day a fairly competent technician could do, because I think the time factor is fairly important.

**J. Eastham**: Yes it is, and it is this factor which provides one of the advantages of the simple combustion technique. An experienced person can prepare the sample (including the weighing, the wrapping and the burning) in 20 min at the most. The

time required for counting the solution will vary and depend on its activity, but then this counting is done automatically in many laboratories. One of the chief difficulties of the Wilzbach technique is that it takes a long time (not in the sense that an operator has to be working continuously but that pyrolysis in the sealed tube with the zinc for a few hours is necessary).

**K. Wilzbach** (United States of America): I can inform Prof. Eastham that we have recently reduced the pyrolysis time to half-an-hour, which helps considerably; an experienced technician at our laboratories can perform analyses by this pyrolysis method in about 20 min working time.

**J. Eastham:** That is quite useful to know. It should perhaps be pointed out that the Wilzbach technique or Schöniger combustion can both be conveniently used for strips cut from paper chromatograms. For very weak activity, the scintillating solvent can actually be placed directly in the side arm of the Schöniger flask, in accordance with our modification.





# PHOTOMULTIPLIERS FOR TRITIUM COUNTING

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## Abstract — Résumé — Аннотация — Resumen

**Photomultipliers for tritium counting.** The use of liquid scintillators in which a tritium-labelled compound is dispersed requires a photomultiplier tube which will give primary signals of amplitude as great as possible. Since the average energy per disintegration is about 5 keV, a large proportion of events will give only one or two photoelectrons from the tube cathode; and these must be distinguished from the thermionic electrons of the tube background.

The paper discusses the development of tubes giving a high ratio of photosensitivity to dark counts and shows that improvements obtained by a combination of processing and geometry changes give satisfactory performance at room temperature with a single tube arrangement. Efficiencies around 15% in toluene solution with a tube background of between 30 and 180 cpm are readily obtainable.

The advantages of cooling and the problem of obtaining the best performance from a coincidence arrangement, with particular reference to the phenomenon of "talk back", are discussed.

The fundamental aspects of dark emission in photomultiplier tubes are considered in the light of the discussion, and predictions regarding ultimate performance are hazarded.

**Photomultiplicateurs pour le comptage du tritium.** L'emploi de scintillateurs liquides dans lesquels est dispersé un composé marqué au tritium exige un tube photomultiplicateur qui donne des signaux primaires d'une amplitude aussi grande que possible. L'énergie moyenne par désintégration étant de 5 keV environ, il y aura une forte proportion d'événements pour lesquels la cathode du tube n'émettra qu'un ou deux photoélectrons, qu'il faut distinguer des électrons thermoioniques du mouvement propre du tube.

Les auteurs examinent la mise au point de tubes caractérisés par un rapport élevé photosensibilité/courants d'obscurité et montrent que les perfectionnements obtenus en modifiant à la fois le mode opératoire et la géométrie donnent des résultats satisfaisants à la température ambiante, avec un dispositif à un seul tube. Dans des solutions de toluène, on obtient facilement des rendements voisins de 15%, avec un mouvement propre compris entre 30 et 180 cpm.

Les auteurs examinent les avantages du refroidissement et la manière d'obtenir le rendement optimum d'un montage en coïncidence, compte tenu notamment du phénomène de réalimentation.

Enfin, à la lumière des considérations ci-dessus, les auteurs étudient les aspects fondamentaux des courants d'obscurité dans les tubes photomultiplicateurs, et ils formulent des prévisions au sujet du rendement global que l'on peut atteindre.

**Фотоумножители для счета трития.** Для применения жидкостных сцинтилляторов, в которых распылено соединение меченого трития, требуется трубка фотоумножителя, которая даст первоначальные сигналы как можно большей амплитуды. Поскольку средняя энергия распада составляет около 5 keV, значительная доля ядерных превращений даст только один или два фотоэлектрона из катодной трубки, и они должны отличаться от термоэлек тронов фона трубки.

В докладе обсуждается проблема разработки трубок, дающих большой процент фоточувствительности по отношению к фону, и указывается, что достижения, полученные в результате сочетания обработки и геометрических изменений, дают удовлетворительные показатели работы при комнатной температуре с размещением одной трубки. Эффективность около 15% в растворе толуола с фоном трубки от 30 до 180 cpm (отсчетов в минуту) легко достигается.

Обсуждены преимущества охлаждения и проблема получения наивысших показателей работы при совпадающем размещении с особой ссылкой на явление "talk back".

Основные аспекты темновой эмиссии в трубках фотоумножителей рассматриваются в свете вышеизложенной дискуссии, и конечные показатели работы предусмотрены рудно.

**Fotomultiplicadores para recuento del tritio.** El empleo de centelleadores líquidos en los que se dispersa un compuesto marcado con tritio exige un tubo fotomultiplicador que emita señales primarias de la máxima amplitud posible. Como en el tritio la energía media por desintegración es de unos 5 keV, habrá una gran proporción de sucesos en que el cátodo del tubo sólo emitirá uno o dos fotoelectrones, que deben distinguirse de los electrones termoiónicos de fondo.

Los autores estudian la construcción de tubos que se caractericen por una elevada proporción fotosensibilidad/impulsos oscuros, e indican que las mejoras obtenidas gracias a modificaciones combinadas de los procedimientos operatorios y de la geometría permiten obtener un rendimiento satisfactorio a la temperatura ambiente con un dispositivo de un solo tubo. En solución de tolueno pueden obtenerse fácilmente rendimientos del orden de 15%, con una actividad de fondo en el tubo comprendida entre 30 y 180 impulsos/min.

Los autores examinan las ventajas de la refrigeración y el problema de obtener el mejor rendimiento de un dispositivo de coincidencias, con particular atención al fenómeno de la realimentación.

Estudian los aspectos fundamentales de la emisión oscura en los tubos fotomultiplicadores, teniendo en cuenta las anteriores consideraciones, y formulan predicciones acerca del rendimiento global que puede alcanzarse.

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The efficiency of a counting assembly for the scintillation assay of compounds tagged with a low energy beta emitter such as  $C^{14}$  or  $H^3$ , which can be dissolved (or suspended) in a liquid phosphor, is very greatly dependent on the quality of the Photomultiplier tube used. This is illustrated by the bias curves of Fig. 1, which shows the curve given by  $10 \mu\text{C}$  of  $H^3$  in a standard phosphor\* (d), the thermionic electron curve from a tube with a standard S-11 cathode (a) and the much more useful performance of tube made specially for  $H^3$  counting (b) and (c).

It is the purpose of this paper to consider the steps by which acceptable performance has been achieved, to report on results obtained in various designs of counting head and to outline those areas in which improvement may still be obtained.

In a standard\* liquid phosphor, the average energy from a tritium disintegration to give a photoelectron from a semi-transparent Cs Sb cathode with a phosphor vial designed to give effective light coupling to the cathode, is ca. 2500 eV, so a large proportion of the disintegrations will give only a single photoelectron and an appreciable proportion (which turns out to be between 30 and 50%) will fail to give a detectable signal. The rate of emission of thermionic electrons from a 2 in diameter photomultiplier tube with a typical S-11 cathode of photosensitivity  $70 \mu\text{A/lm}$ , which has a peak quantum efficiency of ca. 15% at 4200 Å and a red threshold around 6800 Å is about 30 000 electrons/s at 20 °C and about one tenth of this at -20 °C.

If a tube of this type is to be used for tritium counting in a single tube assembly, (with which we are at the moment solely concerned) it is obvious that a bias point corresponding to a signal amplitude much greater than one electron must be

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\* Toluene + 5 g/l p-terphenyl and 16 mg/l POPOP.

chosen and the counting efficiency will be relatively low. In fact, for a tube background of 1 cpm at 20 °C an efficiency of 0.7% is obtained for a 10 ml sample.

The first step, then, in making a photomultiplier tube more suitable for tritium counting is to modify the cathode processing to reduce the thermionic emission as much as possible without unduly depressing the quantum efficiency of the

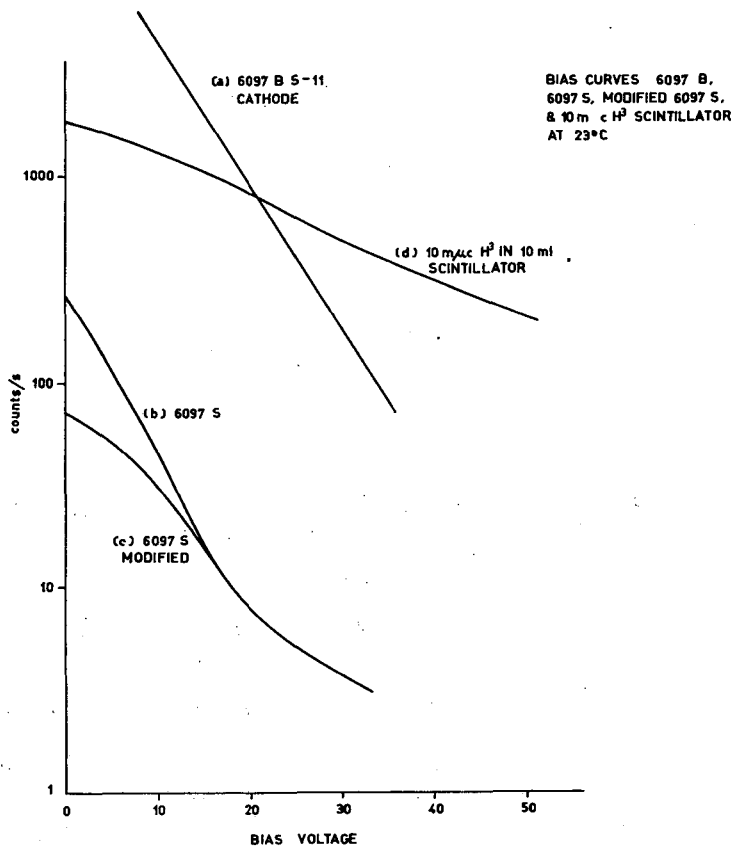


Fig. 1

Illustration of scintillation assay of compounds tagged with C<sup>14</sup> and H<sup>3</sup>.

cathode in the spectral region of interest, which for most phosphors containing POPOP is between 3500 and 4500 Å. Since the high value of thermionic emission from a standard S-11 cathode is associated with an appreciable sensitivity in the red region of the spectrum, our initial criterion for improvement was a decrease in the ratio of red to blue sensitivity and work along these lines was reported at the 1958 Scintillation Counter Conference [1]. It was soon found essential, however, to introduce an operational tritium counting test, since neither the red-blue ratio, nor the tube dark current gave an adequate guide to a tube's performance. This test is carried out in a counting head at room temperature with a sealed 10 ml hemispherical vial containing tritiated toluene phosphor mounted over the tube face, with an interposed shutter assembly (the optical coupling is relatively poor). After an adequate period in the dark (between 1 and 4 h usually), the tube

is adjusted to a standard overall sensitivity and the bias is adjusted until the count rate with the shutter open is an arbitrary figure of 90 counts/sec. The shutter is closed and the tube background rate is measured. The tube performance is then expressed as a ratio, e. g. 90/7 and the smaller the background the better the tube. The correlation between the performance rating and the tube dark current is shown in Fig. 2 and at the present time more than half of the "S" tubes made are

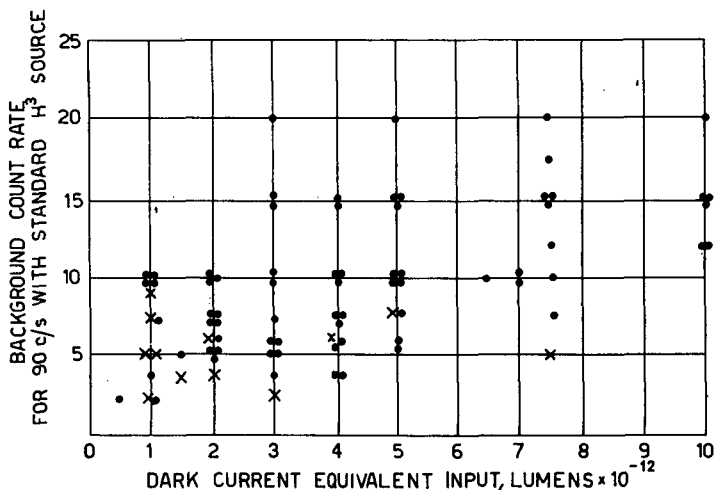


Fig. 2

Correlation between dark current and thermionic background for specified count rate from  $H^3$ -scintillation source in standard test jig.

rated 90/10 or better, of which 15 to 20% are rated 90/5 or better. These latter tubes give efficiencies of 15 to 17% for a tube background of 180 cpm with a 10 ml toluene phosphor sample at 20°C.

In order to put the results summarized above into proper perspective in the field of photomultiplier tubes, it is desirable to consider the characteristics of various dynode structures and their influence on tube background. Three types of dynode structure are in common use; the linear focussed design (used in the R.C.A. 6810A and E.M.I. 9593B), the box and grid structure, (used in the Du Mont 6292 and E.M.I. 9524B) and the venetian blind dynode (used in the E.M.I. 9536, 9514 and 6097). Two types of secondary emitting surface are in general use; Cs Sb, (mainly used in E.M.I. tubes) and Ag-MgO-Cs.

The variation of gain with voltage for representative tubes is shown in Fig. 3 and the increase in gain with a larger number of stages will be noted. This is important, since, in order to reduce the complexity of apparatus used to process the signal after the anode of the photomultiplier tube, it is desirable to operate with as high tube gain as possible, provided this does not in turn produce feedback effects which increase the background signal.

A measure of the feedback stability of a given structure is provided by a plot of anode dark current divided by tube gain, which may be expressed in terms of cathode dark current, or in terms of the input light level to give an anode current equal to the dark current. However expressed, this parameter is found to be roughly independent of tube gain up to some critical value, as shown in Fig. 4.

While the limiting value of gain varies from tube to tube, as does also the cathode dark current, nevertheless typical values may be given to particular tube designs and it is found that the box and grid type of structure has a relatively low limiting gain, around  $5 \times 10^7$ , independent of the number of dynodes (above 10), while the venetian blind structure has a limiting gain which increases with the number of dynodes, values of  $10^9$  with 13 stages being readily obtained. The focussed

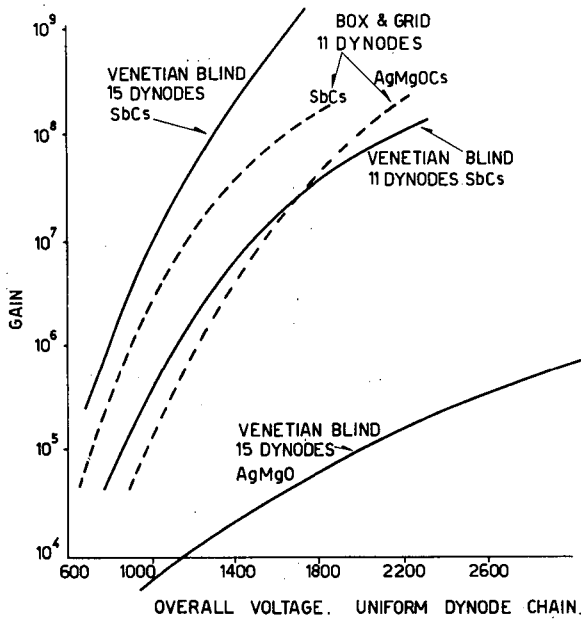


Fig. 3

Gain vs Voltage. Various dynode systems and secondary emitting surfaces.

structure appears to lie midway between the other two designs in its behaviour. (The above comparisons refer to tubes with S-11 cathodes.)

Recently, a statistical study of the variation of dark current among tubes of a given type, has shown that there appears to be a median value characteristic of a given dynode structure, for tubes made with S-11 cathodes of very similar parameters. This is illustrated by the distribution curves of Fig. 5, from which it will be seen that the venetian blind structure gives the lowest value of dark current, while the linear focussed structure is worse by a factor of 20. The fact that the curves appear to be Gaussian when plotted against the log of the dark current suggests that the variation is due to a statistical spread in the work function of the cathode, but there is no obvious explanation for the difference in the median values, since the S-11 cathodes were all very similar. The results are not due in any obvious way to feedback processes, since the tubes were all operating well below the limiting value of gain and it may be that the phenomenon is associated with particular processing techniques which are individual to a dynode design, but the fortunate fact remains that the venetian blind structure, with which E.M.I. has most experience, appears to be very suitable for low dark current tubes.

When tubes are made with "S" cathodes, the dark current is reduced by a factor of 10 or more and it is found that the  $1\frac{1}{2}$  in diameter 9524 S box and grid tube

(with Cs Sb dynodes) becomes very competitive with the 9514 S, only partly due to its smaller cathode area. This reinforces the suggestion that the difference shown in Fig. 5 may in part be due to processing.

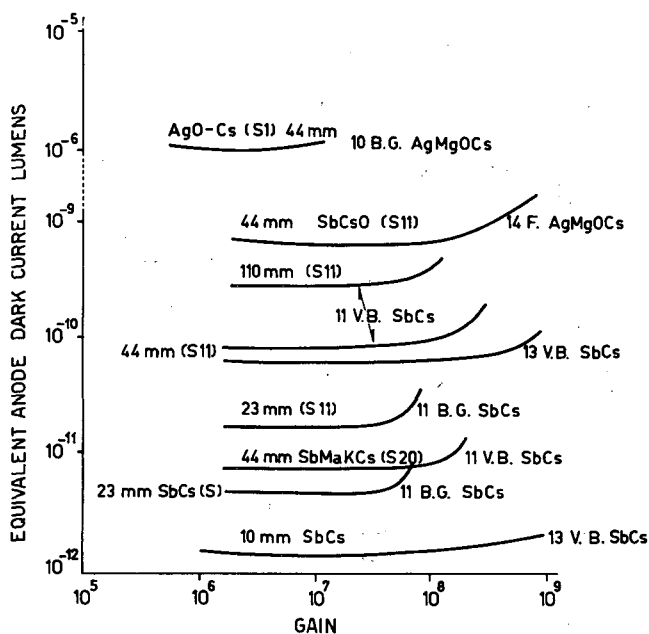


Fig. 4

Dark current at 23°C vs gain.

(Cathode size and type; dynode type and number, as indicated)

Typical sensitivities are:

{	S. 11	60—70 $\mu\text{A}/\text{lm}$ ,
	S.	40 $\mu\text{A}/\text{lm}$ ,
	S. 1	15—30 $\mu\text{A}/\text{lm}$ ,
	S. 20	120—140 $\mu\text{A}/\text{lm}$ .

A further observation relating to dark current is illustrated in Fig. 6 [2]. A tube was fitted with a fine grid parallel and close to the cathode so that a small negative potential difference sufficed to bias off electrons from the end window deposit. Under these conditions it was found that whilst 92% of the anode current produced by illumination of the cathode was cut off, only 14% of the dark current was affected, showing that the major part of the tube background was generated by regions of the cathode-D1 space which were of little utility for the production of photoelectrons. This result was not entirely unexpected, since the production of a uniform deposit of antimony on the window requires that the source of this material be situated in a position ideally suited for coating the walls of the cathode screen with antimony, which will absorb caesium to become an efficient generator of thermionic electrons.

Various artifices have been considered for the reduction or elimination of this undesirable wall coating and in recent months an ingenious arrangement has been developed by V. A. Stanley, at Ruislip. This consists of lining the cylindrical wall with a fine mesh, of small shadow area, spaced away by a millimetre or so.

A small amount of Sb is deposited on the inner facing of this mesh but the greater part passes through onto the wall of the tube. After sensitization, the small area of Cs Sb on the mesh can emit electrons into the C-D1 space for collection into

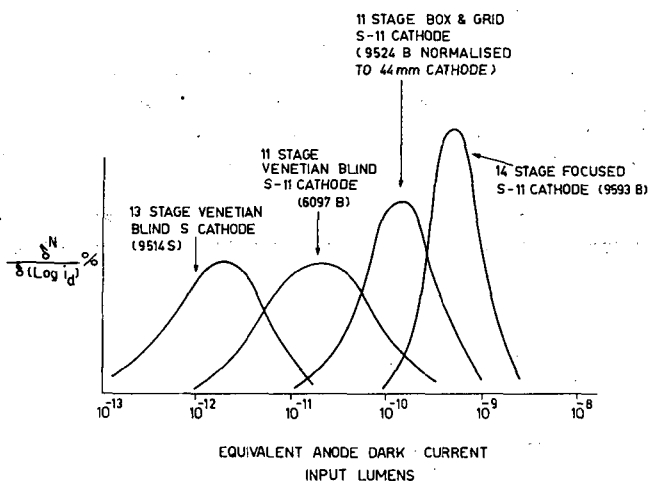


Fig. 5

Distribution curves of dark current for various tube types.

the first dynode, but the electrons from the wall coating are biased back by the contact potential between the suitably chosen mesh material and the cylinder of the cathode screen.

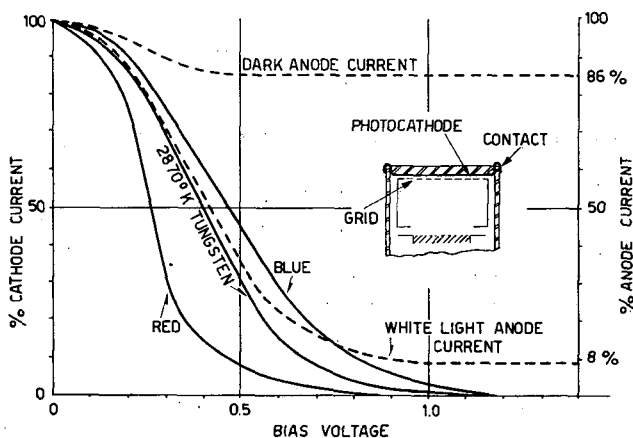


Fig. 6

Characteristics of 6097 with grid control of cathode emission.

The electrons bias curves of tubes of this type have an unexpected shape. In place of the nearly linear relationship between amplitude and log-count-rate, exemplified by curve (b) of Fig. 1, which is found with a conventional "S" cathode

tube, a pronounced fall-off in the number of counts at low amplitude is observed, (curve (c), Fig. 1), although at higher amplitudes the two curves are similar. This suggests that the majority of the thermionic electrons from the tube wall are incident on D1 in a position which gives a lower value of stage gain than those coming from the cathode, while a proportion may skip D1 and produce still smaller pulses from D2, so that the linear curve (b) is, in fact, made up of superposed distributions similar to curve (c), but having a much wider statistical variation due to the inclusion of many signals of amplitude down to a fraction of one secondary electron, in place of the median value of 5 given by electrons from the cathode. In fact, analysis of the two curves shows that the average D1 gain for curve (b) is only half of that for curve (c).

We are now in a position to consider measurements on various photomultiplier tubes, both in special test gear and in various tritium counting assemblies.

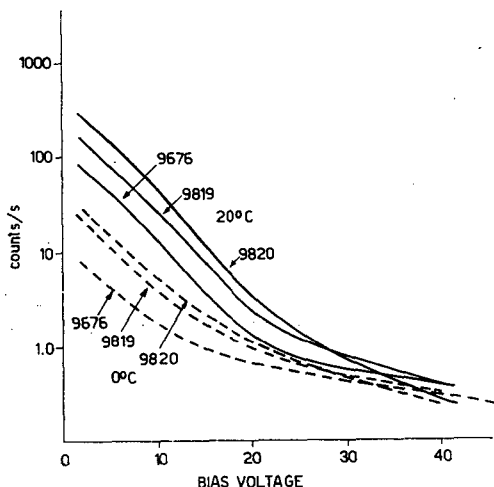


Fig. 7

Tube background at 0°C and 20°C 9524 S No. 9676, 9819, 9820.

Fig. 7 shows bias curves of the tube background for three 28 mm diam. tubes type 9524 S. It will be seen that cooling from 20°C to 0°C reduces the thermionic emission, that is to say the count rate at zero bias, by a factor of about 5. An interesting point will be seen from the curves at larger values of bias, namely that there is a "tail" which is hardly affected by cooling. Fig. 8 shows bias curves at

TABLE I  
POTASSIUM CONTENTS OF VARIOUS WINDOWS

Material	% Potassium*
Quartz	0.003%
Standard Pyrex	0.008%
Standard Lime Soda	0.014%
Jena Glass	6.4%

\* Flame spectrophotometer measurements



room temperature taken on two 50 mm diam. tubes type 6097 S in which one tube has a normal lime soda glass containing ca. 0.014%  $K_2O$ , while a tube, No. 15133, made with a Jena glass containing 6.2% potassium (Table I) is found to have a very high level of counting rate in this large amplitude "tail". The difference in potassium content between the two windows would give a beta particle disintegration rate of about 15/s and this would correspond fairly closely with the difference in level between the two large amplitude "tails", assuming that 50% of the disintegrations gave a detectable pulse. The presumption is that the large amplitude "tails" are due to Cerenkov or fluorescent pulses in the glass, due to either

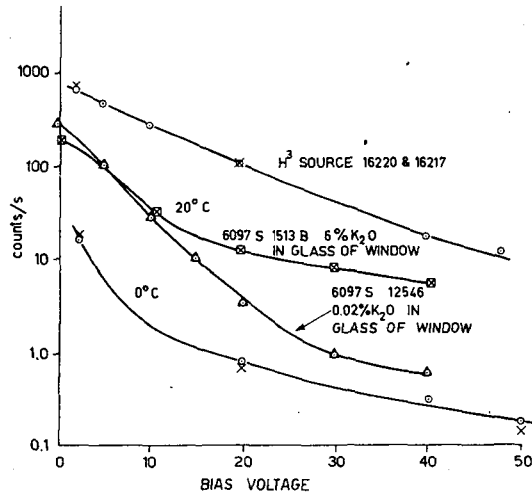


Fig. 8

Bias curves of 6097 S. tubes at 20°C showing effect of  $K_2O$  in glass.

beta particles from potassium and the radium which is a contamination in most glasses or to electrons from scattered gamma rays, while a small proportion, which may be of the order of a few counts per minute, will be due to Cerenkov pulses from cosmic radiation passing through the window. This hypothesis is confirmed by the measurements shown in Fig. 8 on two tubes with lime soda windows of half the normal thickness (Table II).

TABLE II  
ACTIVITY FROM CERENKOV PULSES DUE TO COSMIC RADIATION

Window		Counts/s at 40 V bias. 0°C
Lime Soda	2.5 mm	$0.45 \pm 0.04$
Lime Soda	1.25 mm	$0.29 \pm 0.03$
Tubes normalized to same counting efficiency for $H^3$ at 20 V bias		

Turning now to the low amplitude pulses which are almost certainly due to thermionic electrons, it will be seen that the zero bias count rate in "S" cathode tubes may lie between 300/s and 70/s over the majority of tubes, while just

occasionally a tube is found to have a count rate as low as 36 cps after a long period of storage in the dark. This phenomenon of improvement by dark storage can be most important in tubes of this type and some quite marked effects may

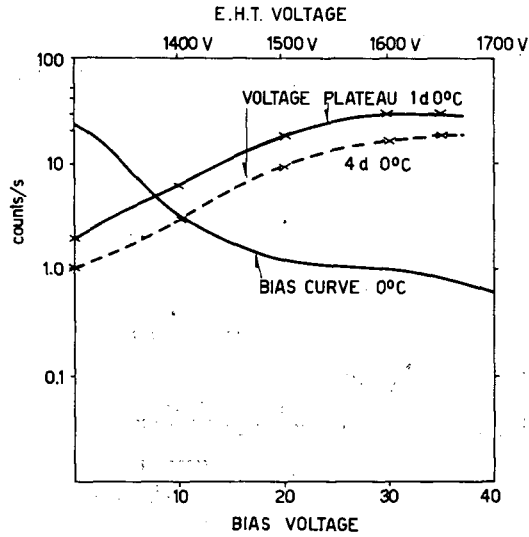


Fig. 9

Quartz window 13 stage tube. 6255 S 5635 tested at  $0^{\circ}\text{C}$ .

often occur. Fig. 9 shows a bias curve at  $0^{\circ}\text{C}$  for a quartz window tube type 6255 S and also shows two E.H.T. plateaux taken over an interval of 3 d. The fact that a plateau of count rate versus voltage is obtained shows that the number of electron

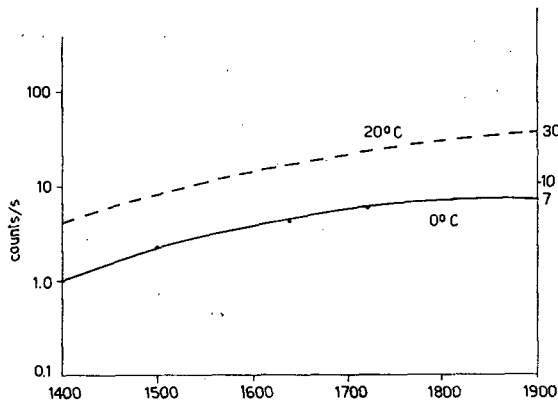


Fig. 10

E. H. T. plateau (Panax) 6097 S 13054; tube background.

pulses of very low amplitude is very nearly zero. A plateau of this kind is not obtained in every tube and is usually not obtained at room temperature. Fig. 10 shows two plateaux taken on a 6097 S which are, perhaps, an exception to this

rule and which represent the tube having the lowest electron count rate of any which we have observed in our series of measurement. At 0°C the electron count rate was down to 7 cps in a counting head operated by Panax Ltd.

The results described above have been repeated on the 50 mm diam. tubes over a range of cathode to D1 voltages from 50 to 150 V and also over a range of E.H.T. voltage from 1250 V to 1750 V (with corresponding variation of amplifier gain), without significant variation in the shape of the bias curves. This latter test is a very sensitive check that no appreciable feedback effects are occurring with the tubes.

When these tubes are operated in a single tube arrangement for tritium counting, the following results are obtained.

In Fig. 11, bias curves taken on a 6097 S with a sealed toluene source show the

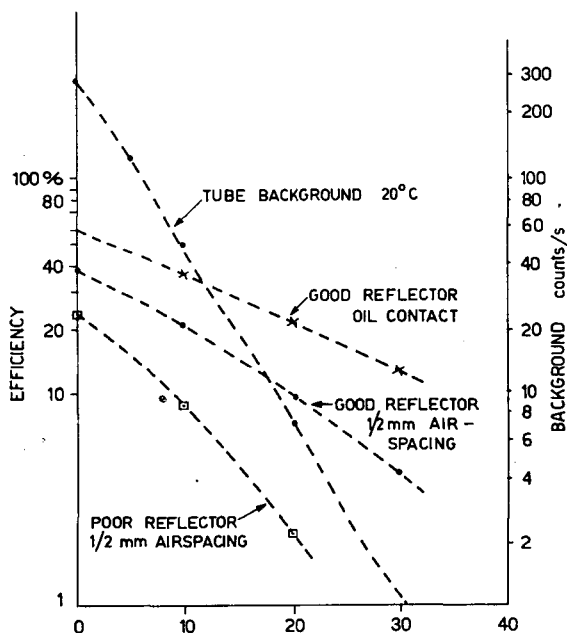


Fig. 11

Effect of source reflector and optical contact 6097 S.

effect on counting efficiency of the quality of the reflector surrounding the hemispherical upper surface of the vial and also of the desirability of making good optical contact between the window of the vial containing the phosphor and the window of the photomultiplier tube.

Fig. 12 shows a plot of tritium counting versus tube background at 20°C obtained at the Thornton Research Centre of the Shell Petroleum Company. Using a standard -6097 S (rating 90/7), a limiting efficiency of about 48% is obtained with a tube background of 200 counts/sec and 14% for 3 counts/sec. Using a modified tube with a mesh mounted around the cathode screen as described above, the background rate for efficiencies below 25% is about the same as for a standard 6097 S, but above this level the effect of reduction in the small pulse background becomes very noticeable and a limiting value of 52% for 70 counts/sec is obtained.

Fig. 13 shows the results obtained by Ekco Nucleonics, using a 9514 S in an arrangement similar to that of the Shell counting head but cooled to  $-20^{\circ}\text{C}$  and having better optical coupling. The limiting efficiency, using a tritiated toluene sample, has now increased to 64% for a tube background of 10 cps, while at 3 cps the efficiency is ca. 50%.

Fig. 14 shows similar curves obtained by Nuclear Enterprises of Edinburgh, using a 9524 tube of 28 mm diam. Fig. 15 shows a bias curve of this arrangement which differs from those mentioned previously, in having a cylindrical vial of height rather greater than its diameter and uses a newly developed phosphor type N.E. 213. The limiting efficiency is 64% at about 1 cps and is 20% at 0.15 cps from the tube. The tube of Fig. 10 gave a plateau at an efficiency of 48% in the Panax head, with a background of 7 cps at  $0^{\circ}\text{C}$ .

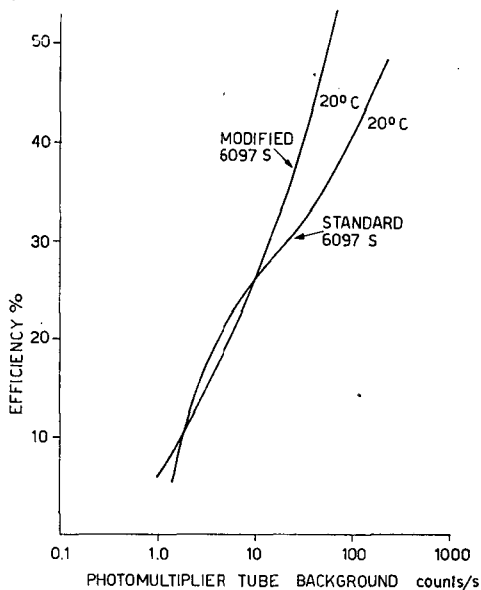


Fig. 12

Shell counting head.

$\text{H}^3$  counting efficiency vs tube background.

$20^{\circ}\text{C}$  10 ml scintillator hemispherical vial.

Amersham hexadecane—1:2T in toluene + 5 g/l p-terphenyl + 16 mg/l POPOP.

From the above it will be seen that for a single tube assembly, operating with an efficient phosphor and vial assembly, the limiting efficiency for  $\text{H}^3$  counting lies between 48 and 64%. In all of the above measurements great care was taken to ensure that measurements were not falsified by phosphorescence of vial or phosphor. This was done by handling in light shields or dark rooms and by the use of identically handled blanks.

The disturbing effects of phosphorescence may be sufficient to demand the use of a coincidence arrangement for their elimination, particularly with some types of sample. From the data given above, we can see that a vial tightly coupled to two photomultiplier tubes, so that the light from a scintillator is shared equally between the two cathodes, will give a maximum efficiency for  $\text{H}^3$  in toluene of

between 25 and 40% (single tube efficiency squared). Any reduction in the optical coupling will markedly reduce this efficiency.

The fact that two tubes are "looking" at each other now immediately brings in the complication of tube interaction and this is considered in an accompanying paper by CAMERON and BOYCE [3]. The general conclusions which would seem to be in accord with the observations reported above and with those of KAUFMAN *et al* [4], is that a very large part of the coincidence interaction is due to light pulses originating in the window of the photomultiplier tube, of Cerenkov or fluorescent origin. Lowest interaction rates are found with quartz window tubes.

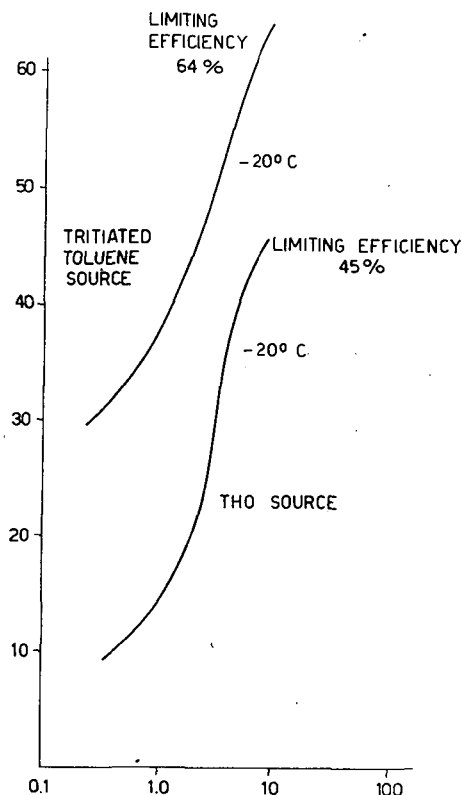


Fig. 13

Ekco tritium counter.

H<sup>3</sup> efficiency vs background; 9514 S photomultiplier tube; 10 ml scintillator; hemispherical vial, 50 mm diam; photomultiplier tube; E.H.T. 1500 V  $\times$  1000 gain amplifier.

At optimum working point ( $\max R_S^2/R_B$ )

Background total  
photomultiplier tube

Tritiated toluene	36%	5 counts/s	1.5 counts/s
THO	38%	12.6 counts/s	4.5 counts/s

One other aspect of tubes which must be examined in connection with coincidence arrangements is a possible advantage of tubes with tri-alkali cathodes (S-20) such as E.M.I. 9558 B. These have high photosensitivities with up to 20% quantum

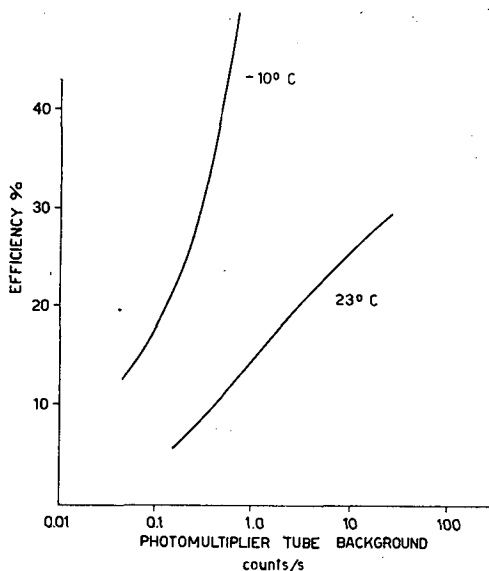


Fig. 14

Nuclear Enterprises tritium counter.

H<sup>3</sup> counting efficiency vs tube background; N.E. 5503 and 9524 A.; 15 ml scintillator cylindrical vial; 28 mm diam. photomultiplier tube.

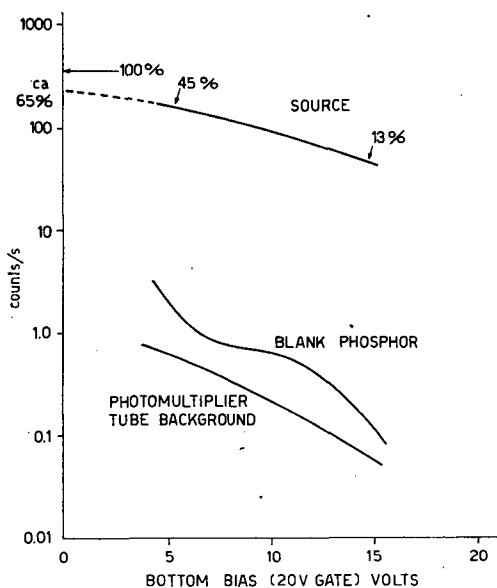


Fig. 15

Bias curves - N.E. 5503 and 9524 A.

Source 10  $\mu$ C H<sup>3</sup> in 15 ml; N.E. 213 scintillator vials-silica; N.E. 5503 shielded head; operating temperature -10°C; N.E. 5202 amplifier gain 5000; 9524 A No. 7141 E.H.T. 750 V; bias curves taken with 20 V gate.

efficiency in the blue and lower thermionic emission than an S-11 cathode, but higher than an "S" cathode.

Tested in our single tube head, such tubes have been mostly rated at 90/25, which compares unfavourably with the modern specially made "S" cathode tubes, but a tube selected for low red sensitivity gave the bias curves of Fig. 16 and a good

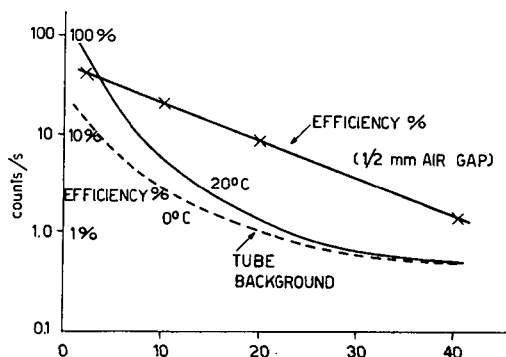


Fig. 16

Tube background and counting efficiency; trialkali cathode 9558/5476.

rating of 90/4. This suggests that the thermionic emission rate of the tri-alkali cathode can be much lower than has previously been reported. The extended spectral response particularly on a tube with a quartz window should recommend these tubes for work on new phosphors.

### Conclusion

At the present moment, photomultiplier tubes are available capable of giving counting efficiencies for 10 ml samples of tritiated toluene phosphors of between 10 and 15% with a tube background of 3 counts/s at 20°C and of 50 to 60% for this background at -10 to -20°C. At this reduced temperature, 10% is obtainable with tube backgrounds of only a few counts per minute.

Some work remains to be done to improve the performance of tubes in coincidence arrangements but significant improvements are obtained by the use of tubes with quartz windows.

### ACKNOWLEDGEMENTS

We are indebted to our colleague Dr. E. E. Thomson for the close collaboration which he afforded us in many aspects of this work and also to our very good friends at Panax, Shell, Ekco and Nuclear Enterprises for the information contained in Figs. 10 to 15. Messrs. Boyce and Cameron at AERE have very kindly allowed us to quote results from their work and thanks are also due to the Directors of E.M.I. Electronics Ltd., for permission to present this paper.

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## DISCUSSION XV

**B. Gordon** (United States of America): I would like to compliment E.M.I. on its careful work. I might point out that in our laboratory we have been using an RCA polyalkali tube which also seems to have a plateau in the noise region but is not as flat over the extended region as the one described in this paper. I wonder whether Mr. Sharpe has any opinion as to what would happen to the shape of the bias curves if he substituted a polyalkali cathode for the cesium antimony one now in use.

**J. Sharpe** (United Kingdom): We have done some work on multialkali cathode tubes. We haven't taken any HT plateau on the bias curves and wouldn't expect a very good one. But the bias curves do, in fact, reproduce all the characteristics of the cesium antimony photocathode and, oddly enough, the efficiency obtained is very much the same. Of course, this is probably because we selected a tube having rather poor characteristics from the multialkali point of view — in other words, one with a rather low red sensitivity and a reasonable blue sensitivity. In general, however, we find that the tubes with multialkali cathodes do not behave as well as those with the modified cesium antimony cathodes.

**P. Holton** (United Kingdom): For the past year I have been grading tubes by tritium counting and I would agree with Mr. Sharpe that such tubes can only be graded by applying a tritium counting test. However, in the interests of all users, I think some effort should be made to standardize the figure of merit. Assuming for the moment that the bias curves are straight lines on the log paper, one can construct from them noise-count versus counting-efficiency curves for different tubes, as the speaker has done. I have found that if, on a graph of this sort, one plots a line of constant noise counts per fractional counting efficiency (e.g. 5 cps/10% counting efficiency), each line corresponding to a photomultiplier will cross this line at a constant ratio. If one then quotes the counting efficiency at which the line is crossed, the photomultipliers are arranged in order of merit. Assuming for the moment that various photomultiplier devices for the counting of tritium can be standardized, say, at the place of manufacture, a line such as I have described could be used for purposes of correspondence and the efficiency described by citing an agreed line. Would Mr. Sharpe be willing to consider a system of this sort for attaching merits to tritium counting tubes?

**J. Sharpe**: I think I would need further information on the rather complicated procedure which Mr. Holton has suggested. At present, we believe that information on the following parameters is required: the value — at a given temperature — of the dark count at zero bias, i.e. the total number of electrons arriving at D1; the effective quantum efficiency of the photocathode; and lastly, the magnitude of the dark count at zero bias, i.e. the total number of electrons arriving at D1; using photomultiplier tubes in tritium counting, each requiring rather different optimization of the two parameters. I do agree, however, that some uniform method of presentation would be extremely useful so far as tube users are concerned, although at the moment I do not quite know how this could be achieved.

**P. Ayres** (United Kingdom): Mr. Sharpe has quoted values for counting efficiency and background for certain photomultipliers in single tube systems. Since the backgrounds given are rather high, the efficiency value becomes more critical



when comparison of counting methods for tritium is involved. The relatively recent acceptance of tritium as a tracer is due mainly to the difficulties initially encountered in measurement. It would therefore be very desirable to have an indication of how the efficiencies given are determined and also of the reliability of the standards used.

**J. Sharpe:** The figures we have used are based on Amersham hexadecane, in standards prepared by the Shell laboratory at Thornton in Cheshire, and sub-standards produced by Ekco and by Panax in the United Kingdom. As far as I can tell from discussions with other people, the limiting efficiency, for which I cited a figure at about 60%, appears to be reasonably well borne out for 10 ml of tritiated toluene phosphors in something like hemispherical vials although — depending on the experimental details — there will of course be some significant variation.

**A. Nir (Israel):** I have a few questions for Mr. Sharpe. First, as regards the real significance of the differences in the dark current for photomultiplier grid structures: Is this a real difference or just a difference in manufacture? Did you, for example, try to mount the 6810 grid on your photo-cathode? Second, in a comparison of tritium bias curves with noise bias curves, should not the tritium counting efficiency be specified so that the multielectron component in its spectrum can be estimated? The bias curve has no absolute significance: it depends on the efficiency and the multielectron component. Third, have you any ideas about the mechanism and origin of the multielectron, or higher energy component of the noise spectrum when the  $K^{40}$  is subtracted?

**J. Sharpe:** On the first point, I think I mentioned our view that the variations in structure must be due to some processing difference in the manufacture of the tubes. I therefore agree that these differences are not likely to be really fundamental, providing that the dark counts are measured on the flat portion of the dark count characteristic. The methods used for obtaining the correct proportioning between photosensitivity and gain will vary from one manufacturer to another and from one tube type to another. On the second point, I agree absolutely that bias curves without tritium efficiencies can be very misleading. However, a good deal of information on the subject — which I could not present for reasons of time — is contained in the paper. A tube having very low thermionic emission but zero quantitative efficiency is quite useless. We have made some tubes of this kind. They are very interesting but of no value. As to the third point, we believe that this component must, to a large extent, be due to activity within the glass, or to fluorescent or Cerenkov pulses produced by activity outside the glass. I believe that the paper of Boyce and Cameron in these proceedings includes some relevant figures. We see no evidence of any feedback origin for this, because when we measure tubes at different voltages, the bias curves, when normalized, lie very closely on top one another. Of course, I am referring only to the tubes that we have measured. I believe that others have found differences in this respect but these, again, are almost certainly a function of the processes. I suppose the short answer to Dr. Nir's question is that we still do not know the whole story.

**R. Hours (France):** Could Mr. Sharpe provide some more details about the stability of the background pulses? Do they follow the normal laws of statistical distribution? Are there sometimes parasite pulses of various origin which could impair background stability, especially in the measurement of tritiated water in which light pulses are very small and lead to the emission of 1–2 photoelectrons? This is of fundamental importance in estimating the merits of various 1-phototube or 2-phototube coincidence systems having a figure of merit of the form:

$$\frac{\text{Efficiency} \times \text{Sample Volume}}{\sqrt{\text{Background}}}$$

**J. Sharpe:** Provided that we operate the tubes well away from the knee of the dark current curve and with the envelope at the same potential as the cathodes, we find that extremely good reproducibility of the noise pulses is obtained, as is evident by the plateau which we measured. But if operations are carried out close to the dark current knee, a burst of pulses can occur perhaps every few minutes and these will certainly upset the system.

**B. Gordon:** Could any reduction in Cerenkov effects be expected if the envelopes of the tubes were made either of dark glass (in order to absorb any photons produced by the potassium-40 or from cosmic sources) or possibly of plastic or some low activity metal? It seems to me that if that were possible you might be able to avoid what is probably one of the major components of noise and what appears to be a major problem in the construction of such tubes.

**J. Sharpe:** This question has been considered in other connections, notably in the manufacture of photomultiplier tubes for low background gamma-ray counting, where the possibility of using copper envelopes has been raised. However, it has been our experience that photomultiplier tubes are very sensitive to changes of this kind, and that the achievement of stability is critically dependent on the correct potential distribution on the inside wall. Our experiments with unipotential conducting coatings on the inside wall of photomultiplier tubes have been extremely disappointing. Of course, there must always be a window of the correct transmission and, generally speaking, the problem in that case is not what kind of glass one would like to use but the kind of glass that will be compatible with the manufacturing techniques (such as metal to glass sealing, etc.). The new Corning low activity glass is extremely interesting to us in this respect and we are hoping to get some for a trial envelope. The important consideration will be the absence of radium. If it is absent, those tubes should then be at least as good as the quartz window tubes and probably even better, because the entire envelope can be made from the low activity material, eliminating the need for graded seals down to normal glasses, as in the case of the quartz tube.

**C. Brooke (Belgium):** Has the speaker any explanation for the rather wide discrepancy between dark current and dark count in the tubes (cf. Fig. 2)?

**J. Sharpe:** I think that one reason for it is the fact that the counting efficiency for tritium is a function of the photosensitivity of the cathode and it is possible to have a tube with a very high photosensitivity and a rather higher value of dark current. This gives a better result than a tube with a low value for both dark current and photosensitivity. We do not think that this is the whole answer and the matter is still being investigated.

**R. Lloyd (United Kingdom):** Cameron and Boyce have shown in their paper [p. 231] that a major part of the photomultiplier background in coincidence arrangements is due to the radioactive content of the window, and that the window is itself also a scintillator. This agrees with Mr. Sharpe's findings that the tail on the noise/bias curve is due to radioactive contamination of the window. We have shown that Chance OX7 glass is non-photophorescent, even less so than quartz. If this glass is also nonfluorescent, as it might well be, then it should be possible to construct a photomultiplier window which has greatly reduced light emission, despite the fact that it is slightly active. Moreover, if the reason for the lack of luminescence in OX7 could be found, it might be possible to construct a clear window with these properties, either by adding a quencher or by omitting the luminescence centre.

**R. Hours:** In Mr. Sharpe's pre-print, the potassium content of the phototube quartz windows is shown as being higher than that of standard "Pyrex" glass. This is rather surprising.

**J. Sharpe:** The correct figures are as follows: for the quartz: 0.008 and for the standard "Pyrex": 0.05. We assume that the potassium in the quartz was due to some contamination of the water during the geothermal formation of the quartz. The measurements were done with a flame photospectrometer and we have fair confidence in them.

**F. Begemann** (Federal Republic of Germany): You are probably aware that synthetic quartz is now available. I would assume that its content of all types of contamination is rather low.

**J. Sharpe:** Yes, this is a material which we are going to use instead of the fused quartz in future tubes.



# A LOW-BACKGROUND LIQUID-SCINTILLATION COUNTER FOR THE ASSAY OF LOW-SPECIFIC-ACTIVITY TRITIATED WATER

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Abstract — Résumé — Аннотация — Resumen

**A low-background liquid-scintillation counter for the assay of low-specific activity-tritiated water.** In liquid-scintillation counting of tritiated water single photomultiplier counters and coincidence systems offer comparable sensitivities. To investigate low level counting a coincidence system was selected to avoid uncertainties in the background due to single photon events arising from phosphorescence and chemiluminescence in the solution.

With this system the background was found to be due largely to light originating in the photomultiplier photocathode. Using two photomultipliers with "Pyrex" photocathodes in contact in an 8 in thick iron shield experiments were conducted to determine the relative importance of the following possible courses of background:

- (a) Ionization and excitation of residual gas and of the semi-conductor dynode surfaces, particularly in regions where the current density is greatest.
- (b) Sparking, electroluminescence and field emission.
- (c) Positive ion feedback to the photocathode causing secondary electron emission.
- (d) Operation of the photocathode window itself as a phosphor for cosmic radiation,  $K^{40}$  beta particles or radiation from uranium daughter products.

In particular it was found that contribution (c) was significantly lower than was previously supposed. Methods of minimizing these effects, including the use of quartz photocathodes, and special photomultipliers were investigated.

In the finished design of counter the minimum detectable specific activity with a counting time of 30 min. is  $6 \times 10^7$   $\mu\text{C/ml}$ .

**Compteur à scintillations à liquides, à faible mouvement propre, pour le dosage d'eau tritiée en faible activité spécifique.** Dans le dosage de l'eau tritiée au moyen d'un compteur à scintillations à liquides, les compteurs à photomultiplicateur unique et les ensembles à coïncidences présentent une sensibilité du même ordre. Pour faire des recherches sur la mesure des faibles activités, les auteurs ont choisi un dispositif monté en coïncidence, afin d'éviter les incertitudes dans le mouvement propre causées par l'apparition de photons isolés, dus à la phosphorescence et à la chimiluminescence de la solution.

Dans ce dispositif, on a constaté que le mouvement propre provient surtout de la lumière qui émane de la photocathode du photomultiplicateur. En utilisant deux photomultiplicateurs à photocathode en pyrex, en contact dans une protection en fer de 20 cm, on a procédé à des expériences pour déterminer l'importance relative des phénomènes ci-après pouvant constituer le mouvement propre:

- a) Ionisation et excitation des gaz résiduels et des surfaces des dynodes à semi-conducteurs, notamment aux endroits où la densité du courant est la plus élevée;
- b) Production d'étincelles, électroluminescence et émission du champ;
- c) Rétroaction positive des ions vers la photocathode, provoquant une émission d'électrons secondaire;
- d) Fenêtre de la photocathode jouant elle-même le rôle de scintillateur pour les rayons cosmiques, les particules bêta du  $^{40}\text{K}$  et les rayonnements émis par les produits de filiation de l'uranium.

Les auteurs ont notamment établi que le facteur c) avait sensiblement moins d'importance qu'on ne l'avait supposé précédemment. Ils ont fait des recherches sur les méthodes permettant de réduire ces effets au minimum, notamment en utilisant des photocathodes en quartz et des photomultiplicateurs spéciaux.

Avec l'ensemble de comptage conçu par les auteurs, l'activité spécifique minimum décelable est de  $6 \cdot 10^{-7} \mu\text{c/ml}$ , le temps de comptage étant de 30 minutes.

**Жидкостный сцинтилляционный счетчик с низким фоном для анализа насыщенной тритием воды с низкой удельной активностью.** При счете жидкостных сцинтилляций насыщенной тритием воды счетчики с одним фотоумножителем и системы совпадений дают показания сравнительной чувствительности. Для исследования счета излучения малой интенсивности была применена система совпадений для того, чтобы избежать неопределенности в фоне, вызываемой изменением одного фотона в результате фосфоресценции и химической люминесценции в растворе.

Было обнаружено, что возникновение фона в этой системе объясняется главным образом действием света, исходящего из фотокатода фотоумножителя. Были проведены эксперименты с применением двух фотоумножителей с фотокатодами Пирекс в контакте с железным экраном толщиной в 8 дюймов для определения относительной важности следующих возможных факторов фона:

а) Ионизация и возбуждение остаточного газа и поверхностей полупроводникового диода, особенно в тех зонах, где имеется самая большая плотность потока,

б) Искрообразование, электролюминесценция и автоэлектронная эмиссия,

с) Обратная связь положительных ионов с фотокатодом, что вызывает вторичную электронную эмиссию,

д) Самостоятельное действие фотокатодного окна подобно люминофору космической радиации, бета-частицам  $K^{41}$  или радиации дочерних продуктов урана.

В частности, было обнаружено значительно меньшее воздействие фактора, чем ранее предполагалось. Были исследованы методы уменьшения этих воздействий, включая использование кварцевых фотокатодов и специальных фотоумножителей.

В окончательной конструкции счетчика минимальная обнаруживаемая удельная активность со временем счета в 30 минут составляет  $6 \times 10^{-7}$  микроюри на миллилитр.

**Contador de centelleador líquido de reducida actividad de fondo para el análisis de agua tritiada de baja actividad específica.** Cuando se trata de efectuar el recuento de agua tritiada por centelleo de líquidos, los contadores de fotomultiplicador único y los dispositivos de coincidencias presentan sensibilidades comparables. Con el fin de efectuar estudios sobre la medición de bajas actividades, los autores eligieron un sistema de coincidencias para evitar la incertidumbre en lo que respecta a la actividad de fondo debida a fotones aislados emitidos en virtud de la fosforescencia y quimioluminiscencia de la solución.

Los autores comprobaron que, en este sistema, la actividad de fondo proviene principalmente de la luz que emana del fotocátodo del fotomultiplicador. Utilizando dos fotomultiplicadores con fotocátodos de pyrex en contacto, encerrados en un blindaje de hierro de 20 cm de espesor, hicieron experimentos para determinar la importancia relativa de las siguientes posibles causas de la actividad de fondo:

а) Ionización y excitación del gas residual y de las superficies del dínodo semiconductor, especialmente en las regiones en que la densidad de corriente es máxima;

б) Formación de chispas, electroluminiscencia y emisión de campo;

с) Realimentación de iones positivos al fotocátodo, que provoca una emisión de electrones secundarios;

д) Funcionamiento de la propia ventana fotocatódica en carácter de "fósforo" para la radiación cósmica, las partículas  $\beta$  del  $^{40}\text{K}$  o las radiaciones de los productos de filiación del uranio.

Los autores comprobaron que, en particular, el factor c) interviene en una proporción mucho menor que lo que se había supuesto. Estudiaron métodos para reducir a un mínimo estos efectos, incluyendo el uso de fotocátodos de cuarzo y fotomultiplicadores especiales.

Con el dispositivo diseñado por los autores, la mínima actividad específica detectable, con un tiempo de recuento de 30 min, asciende a  $6 \times 10^{-7} \mu\text{curies/ml}$ .

## 1. Introduction

For the measurement of tritium in water, both single photomultiplier and coincidence liquid scintillation counting systems are used. Although comparable sensitivities can be obtained from these systems, the coincidence system was selected for a low background counter as it has the advantages of insensitivity to phosphorescence and chemiluminescence which severely restrict the accuracy of the single photomultiplier system, and it can be operated at room temperature [1, 2].

In the measurement of a low activity sample giving a count rate near to that of background, the fractional error is inversely proportional to the figure of merit  $M$  defined as

$$M = E V B^{-1/2} \quad (1)$$

where  $E$  is the overall percentages efficiency,  $V$  the volume of sample and  $B$  the background count rate [3]. The larger the value of  $M$ , the smaller is the minimum specific activity which can be detected to a given degree of certainty.

The volume of sample normally available is dependent on the application. In medicine and biology,  $V$  is likely to be small. In geological water tracing, for which this particular work is relevant, volumes available are likely to be unlimited and under such circumstances it has been shown that, using photomultipliers with 5 cm diam. photocathodes, the maximum figure of merit is obtained with samples of about 30 ml in 140 ml of phosphor [4, 5]. Although this figure could probably be improved by using photomultipliers of larger cathode area and larger volumes of phosphor, the cost of phosphor then becomes important and it is felt that the 5 cm diam. cathodes are a satisfactory compromise.

To achieve a high value of  $M$ , the phosphor should dissolve a large volume of water and be of high purity to give maximum fluorescence efficiency. The phosphor container should be of optimum shape, have high reflectivity and be optically coupled to the photomultiplier windows. Photomultipliers should have high photocathode sensitivity.

Methods of reducing the background are known and involve using anti-coincidence counters, massive lead or iron shields and materials selected for low natural radioactive content.

This paper presents the results of investigations into the most important factors which determine  $M$  and describes a counting system which detects less than  $10^{-6} \mu\text{C/ml}$  of tritium in a 16 ml sample of water in a counting time of 30 min.

## 2. Apparatus

### 2.1. LIQUID PHOSPHORS

For the measurement of water samples, a phosphor containing alcohol or dioxane is required. The highest reported efficiency for the measurement of tritium in water has been obtained with a mixture of toluene, alcohol, dioxane, PPO, POPOP and naphthalene [6]. However, in water tracing the important criterion is the product of efficiency and volume of water dissolved, and this is maximum using dioxane only as the solvent [4]. Other constituents of the dioxane phosphor, to which can

be added 25% water, are 6 g/l PPO and 100 g/l naphthalene. POPOP is normally added to phosphors as a wavelength shifter but 10 ml samples of the above phosphor with and without 0.3 g/l POPOP gave no significant difference in coincidence count rates measured with a standard deviation of 3%. It was therefore omitted in further measurements.

In this work the dioxane was purified by refluxing over sodium for 1 h filtered and fractionally distilled.

Table I summarizes the effects of different stages in dioxane purification on the efficiency of a coincidence system for a 10 ml sample.

TABLE I  
EFFICIENCY OF DIOXANE PHOSPHOR AT DIFFERENT STAGES OF PURIFICATION

Method of Purification	Efficiency (%)
(a) "Purified" (as commercially available)	$5.0 \pm 0.1$
(b) Reflux over sodium for 1 h and filter	Turned yellow after a few hours
(c) Reflux over sodium for 4 h and filter	Turned yellow after a few hours
(d) Distillation of (a)	$5.3 \pm 0.1$
(e) Distillation of (b)	$6.2 \pm 0.1$
(f) Distillation of (c)	$6.3 \pm 0.1$

It was found that the addition of water to phosphors made from (a) and (d) gave intense chemiluminescence which rose to a maximum (producing approximately  $10^6$  cpm in each photomultiplier) in 10–15 min and then decayed slowly with an initial half value period of about 15 h. This chemiluminescence may be due to formaldehyde which is removed on further purification.

The liquid phosphor having the greatest efficiency is toluene containing

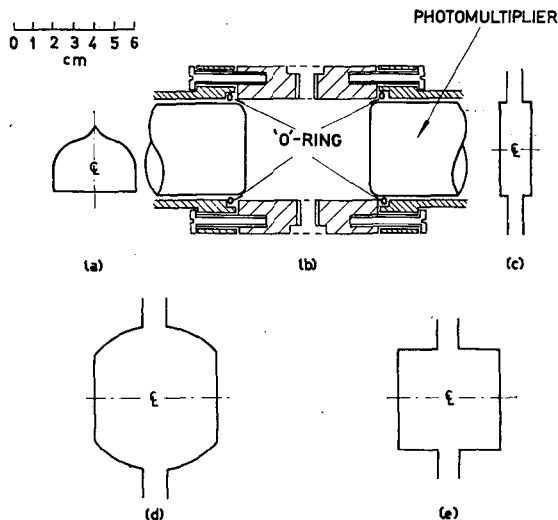


Fig. 1  
Phosphor containers.

3–5 g/l PPO. Although water cannot be introduced directly, it is a simple and stable system and with an absolutely measured activity ( $\pm 5\%$ ) of tritiated toluene added, was chosen as a standard in this work.



## 2.2. PHOSPHOR CONTAINERS

The containers used in experiments to analyse the background and that used in the final low background system are shown in Fig. 1.

Container (a) which is made of "Pyrex", is 5 cm in diameter, flat-bottomed and externally silvered. It was used to hold 10 ml of the 'standard' solution. Container (b) has a volume of 110 ml and is one of a series of duraluminium cylinders of varying lengths having ends closed by the photomultiplier windows and sealed with synthetic silicone rubber "O"-rings. The cylindrical "Pyrex" container (c) has a volume of 50 ml. Containers (d) and (e) are of quartz and the volumes are 220 and 80 ml respectively.

## 2.3. ELECTRONICS

Manufacturers specifications on tubes used in this work are given in Table II.

TABLE II  
PHOTOMULTIPLIER DATA

Number	Photomultiplier*		Photocathode sensitivity ( $\mu\text{A}/\text{lm}$ )	Dark current at 2000 A/lm ( $\mu\text{A}$ )	Photocathode	
	Type	Serial No.			Glass	diam
1	9514 S	5460	32	0.008	"Pyrex"	44 mm
2	9514 S	5475	42	0.14	"Pyrex"	44 mm
3	9514 S	6748	58	0.02	Lime-Soda	44 mm
4	9514 S	6750	65	0.006	Lime-Soda	44 mm
5	9514 S	6902	80	0.006	Lime-Soda	44 mm
6	9514 S	7078	83	0.016	Lime-Soda	44 mm
7	9514 S	6641	45	0.006	Lime-Soda	44 mm
8	9514 S	6703	56	0.012	Lime-Soda	44 mm
9	6255 S	5574	40	0.016	Quartz	44 mm
10	6255 S	5577	38	0.009	Quartz	44 mm
11	6255 S	5625	60	0.014	Quartz	44 mm
12	6255 S	5626	55	0.012	Quartz	44 mm
13	6255 S	5608	58	0.003	Quartz	44 mm
14	6255 S	5629	42	0.015	Quartz	44 mm
15	6260 B**	2462	—	—	"Kodial"	44 mm
16	6260 B**	2752	—	—	"Kodial"	44 mm
17	9524 S	6589	45	0.001	Lime-Soda	23 mm
18	9524 S	—	—	—	Lime-Soda	23 mm

\* E. M. I. Electronics Ltd.

\*\* Obsolete

Tubes 7, 8, 13 and 14 are experimental types fitted with a wire mesh, to reduce thermionic emission from the cathode screen, and a shutter between cathode and first dynode, to block light travelling from the dynodes to the photocathode.

A schematic diagram of the coincidence system is shown in Fig. 2. Pulses from each photomultiplier, after amplification, are fed to high and low level discriminators. The low discriminators bias (2 V) is set to reject amplifier noise (about 1 V). To reduce background from higher energy radiations all coincidences corresponding to large pulses which pass the upper discriminators are deleted by the anti-coincidence unit.

Maximum coincidence count rate was obtained with a resolving time of 0.2  $\mu\text{sec}$  but 0.3  $\mu\text{sec}$  was used in practice to avoid any loss in efficiency. The resolving time of the anti-coincidence unit was set at 4  $\mu\text{sec}$ .

In the experiments to be described, coincidence count rates are specified according to the amplitude range of the pulses to which are due. The following definitions are used:

- 'total coincidence': all coincidence pulses passing the lower discriminators;
- 'limited coincidence': all coincidence pulses with amplitudes between the upper and lower discriminators;
- 'total anti-coincidence': 'total coincidences' minus those coincidences also associated with an external anti-coincidence ring;
- 'limited anti-coincidence': 'limited coincidence' minus those coincidences also associated with an external anti-coincidence shield.

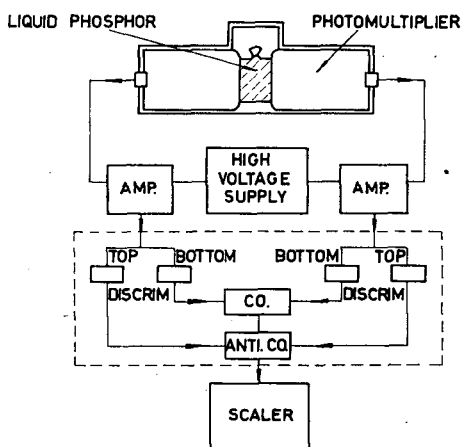


Fig. 2

Schematic diagram of coincidence system.

The cell, phosphor and shielding are specified in each case. Similarly, efficiency is specified as 'limited coincidence efficiency' if it is calculated from the measured 'limited coincidence count rate' and so on.

When using upper and lower discriminators it is possible to select the gain of each channel to give a so-called 'balance point operation' [7] when the efficiency is independent of small variations in gain. For convenience, amplifier gains are fixed and photomultiplier voltages are selected with a cell containing tritium in position, by setting one tube at an arbitrary voltage and plotting the limited coincidence counting rate against the voltage on the second tube, the potential at which the maximum in the curve occurs being chosen as the optimum. The procedure is then repeated for the first tube with the second tube set at its optimum voltage. Under these conditions a change of  $\pm 20$  V in 1000 V does not affect the limited coincidence efficiency.

The bias of the upper discriminator was set at several levels up to the maximum limit of 50 V, and photomultiplier potentials adjusted as above using container (b). The resulting figures of merit are plotted in Fig. 3 as a function of top discriminator bias voltage. The curve is near its maximum when the top discriminators are at 50 V, which is near the limit of linear amplifier output and the maximum setting of the discriminators used.

Although the random coincidence count rate from the photomultipliers is negli-

gible, that from the phosphor has to be measured and, if necessary, subtracted from the sample counting rate. The random rate is conveniently determined by delaying the pulses from one photomultiplier by at least three times the resolving time of the first coincidence mixer ( $0.3 \mu\text{sec}$ ) and a  $1 \mu\text{sec}$  delay was used.

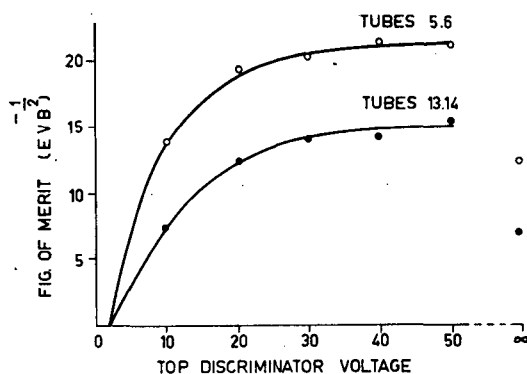


Fig. 3

Variation of fig. of merit with top discriminator voltage.

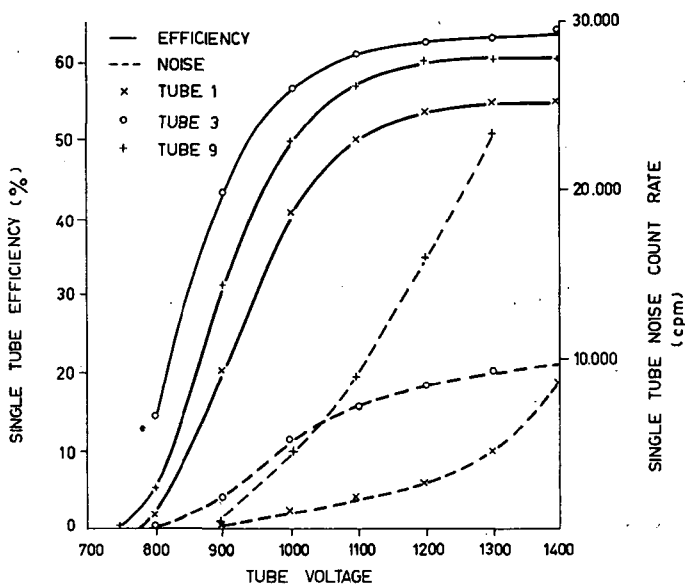


Fig. 4

Variation of single tube total efficiency and noise with tube voltage.

Fig. 4 shows the variation with photomultiplier potential of tube noise and efficiency for the standard source, for some typical photomultipliers. The voltage for balance point operation was found to be about 100 V below the "knee" in the efficiency curve.

### 3. Causes of background counts in a coincidence system

In a coincidence system, background counts may arise either from chance coincidences due to the finite resolving time of the coincidence unit or from genuine coincidences such as occur from light emitted in the photomultipliers and visible to both tubes.

If the resolving time of the coincidence system is  $\tau$ , and the count rates from the separate photomultipliers due to random thermionic electron emission are  $n_1$  and  $n_2$ , the chance coincidence count rate is  $2 n_1 n_2 \tau$ . For selected photomultipliers,  $n_1$  and  $n_2$  are each normally less than 12 000/min at room temperature and as  $\tau$  is 0.3  $\mu$ sec, the random coincidence background count rate is less than one cpm and negligible.

TABLE III  
BACKGROUND COUNT RATE OF A COINCIDENCE SYSTEM  
USING CONTAINER (b) AND TUBES 1 AND 2

Conditions of Measurement	Background count rate (cpm)			
	Coincidence		Anti-coincidence	
	Limited	Total	Limited	Total
With phosphor Unshielded	678	3 670	—	—
In 10 cm Pb shield	$98 \pm 2$	$403 \pm 4$	$96 \pm 2$	$350 \pm 4$
In 10 cm Pb and PTFE liner on cell	$102 \pm 2$	$405 \pm 5$	—	—
In 10 cm Pb and 2.5 cm Hg shields	$75 \pm 3$	$345 \pm 5$	—	—
1 $\mu$ s delay on pulses from one amplifier	$5 \pm 1$	—	—	—
With alcohol				
10 cm Pb shield	$71 \pm 2$	$122 \pm 2$	$66 \pm 2$	$86 \pm 2$
Empty Container				
10 cm Pb shield	$38 \pm 2$	$61 \pm 2$	$34 \pm 2$	$47 \pm 2$
10 cm Pb shield and black paper disc between windows	$2 \pm 0.4$	$0.3 \pm 0.3$	—	—

To estimate the relative importance of the causes of genuine background coincidence counts, the measurements summarized in Table III were made with container (b). A 1 mm thick PTFE liner was used to investigate the importance of surface contamination. This material contains no radioactive contaminants and absorbs alpha particles emitted from the container walls. It was found to increase the efficiency from 6.8 to 7.6% for the dioxane phosphor containing 25% water.

It is apparent that chance coincidences (see 1  $\mu$ sec delay) and surface contamination of the container walls (see effect of PTFE liner) do not contribute significantly to the background count rate. A large proportion (66/96) of the background in the screened system is attributable to light generated in the photomultipliers. This has therefore been investigated as it offers the possibility of reduction in background.

### 3.1. BACKGROUND COUNTS ARISING FROM THE PHOTOMULTIPLIER

Light emission producing background count rate in the photomultiplier may be due to:

- (a) Ionization and excitation of residual gas and of the semi-conductor dynode surfaces, particularly in regions where the current density is greatest,
- (b) Sparking, electroluminescence and field emission,
- (c) Positive ion feedback to the photocathode causing secondary electron emission,
- (d) Operation of the photocathode window itself as a phosphor for cosmic radiation, external gamma radiation,  $K^{40}$  beta particles or radiation from uranium daughter products.

Of these, the only effect which is independent of photomultiplier voltage is (d).

To find the relative importance of these possible causes of background counts, the following experiments were conducted.

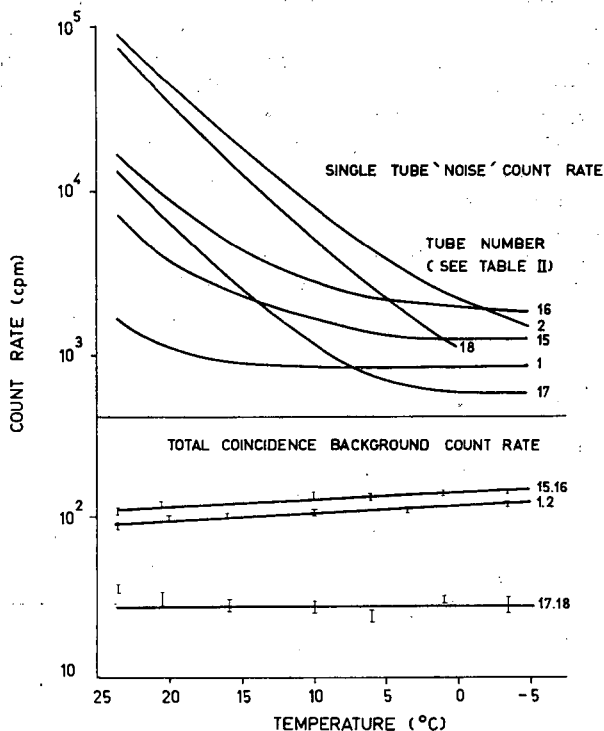


Fig. 5

Variation with temperature of single photomultiplier noise and coincidence count rates.

#### 3.1.1. COINCIDENCE COUNT RATES FROM DIFFERENT TUBES AND AT DIFFERENT TEMPERATURES

The effect of temperature on the coincidence count rate and the variation of total coincidence background count rate from one pair of tubes to another were first investigated.

Pairs of photomultipliers were assembled unshielded, with photocathode windows adjoining and optically coupled with silicone oil. Applied potentials were adjusted

to give an efficiency of 50% for each channel using the standard source. The effect of temperature on the coincidence count rates and on the single tube count rates is shown in Fig. 5.

The coincidence count rate is evidently unaffected by large differences in current density (single photomultiplier noise). It is therefore unlikely to be due either to electrons escaping from the dynode structure and striking the glass envelope, or to positive ion feedback to the photocathode. It is also roughly proportional to photocathode area and does not vary much from tube to tube.

### 3.1.2. BACKGROUND COUNTS CAUSED BY OPERATION OF PHOTOMULTIPLIERS

It is known that with large anode currents, light emission may occur near the anode [8, 9], and this possibility was examined by subjecting the photocathode of a 9514 S tube to a thin pencil light beam which did not reach the final dynodes. By gradually increasing the voltage it was seen that light visible to the dark-adapted, naked eye was predominantly in the vicinity of the anode and last dynode. On increasing the voltage the light spread to preceding dynodes. If a cause of coincidences is light emission at the anode, the most likely path is along the outside of the dynode assembly, as the dynode structure itself is relatively opaque [9]. It has been reported that in 6255 S tubes a large proportion of the light causing background coincidence counts travels along the annular ring outside the photocathode screen [10], but this has not been found on other tubes [4, 11] nor in the experiments described below.

Using a series of black paper discs of differing areas sandwiched symmetrically between two photomultipliers, it was shown that the background coincidence count rate in a 10 cm Pb shield decreased linearly with the masked area, as illustrated in

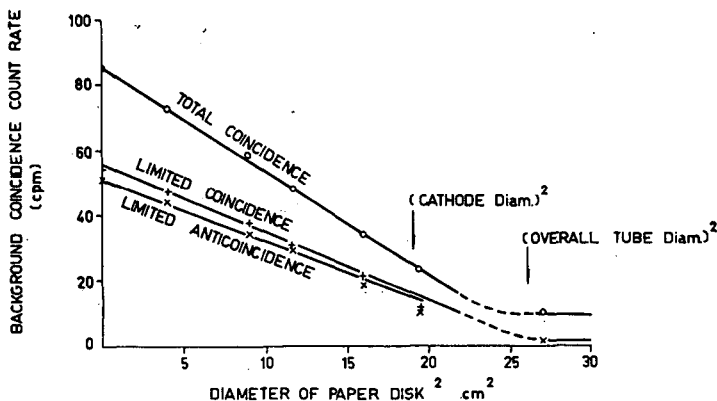


Fig. 6

Variation of background coincidence count rate with masked area of photocathode (tubes 1 and 2).

Fig. 6. As no significant increase was obtained from the outermost area of the window, it was concluded that the light was not all due to operation of the photomultipliers. This conclusion is supported by the curves of Fig. 5 which includes results from photomultipliers 15 and 16 having a black painted neck near the

cathode acting as a light block, and also by the fact that black tape wrapped around the photomultipliers made no difference, although it partially absorbed light internally reflected along the glass.

As an additional verification, tubes 1 and 2 were optically coupled and cooled to  $-5^{\circ}\text{C}$  at which temperature the count rate (c 1000/min) of tube 1 varies little with temperature. The count rate of tube 1 was measured with tube 2 operating for periods up to several hours. On switching off tube 2, the count rate of tube 1 fell by only about 18 cpm and there was no evidence of a surge in count rate on switching on or off. However, even this difference is suspect since after continuous operation for 30 h there was no decrease in count rate of tube 1 on switching off tube 2. Because of this discrepancy, a special cell of triangular cross-section was constructed into which projected the photocathodes of tubes 1, 11 and 12, and which was filled with silicone fluid. The total coincidence count rate between tubes 11 and 12 was  $115 \pm 0.5$  cpm with the normal voltage applied to tube 1 and  $116 \pm 0.3$  cpm with this voltage switched off. Similarly the total coincidence count rate between tubes 1 and 11 was  $114 \pm 1$  cpm and there was no increase when the voltage was applied to tube 12, showing that there was no detectable light generated in the photomultiplier under normal operation.

### 3.1.3. BACKGROUND COUNTS DUE TO CONTAMINATION OF PHOTOCATHODE WINDOWS

Ionizing radiation emitted by radioactive contaminants in the photocathode windows may give rise to light visible to both tubes. Beta particles, for example, will produce Cerenkov radiation and fluorescence in the glass. The most likely contaminants are uranium impurities and  $\text{K}^{40}$  which is present in the  $\text{K}_2\text{O}$  constituent of some glasses. Photocathode windows may be of quartz, "Pyrex", lime soda or "Kodial" glass and  $\text{K}_2\text{O}$  is present in all, except quartz, in proportions usually below 1% by weight. The natural abundance of  $\text{K}^{40}$  is 0.012% and it decays by emitting beta particles of maximum energy 1.33 MeV in 87.7% of its disintegrations. This activity results in the emission of 1740 beta particles/min/g of natural potassium. An average photocathode weighs about 10 g and, if it contains 1% by weight of  $\text{K}_2\text{O}$ , will therefore emit 146 beta particles/min.

Uranium is a possible contaminant in quartz, but as the windows are produced from large single crystals, they are unlikely to contain appreciable amounts of this element.

Window contamination has been shown to contribute about 10 cpm to the background of a single photomultiplier low background counter [12—14]. To estimate the contribution to the coincidence background from window contamination, windows of quartz, "Pyrex", lime soda and "Kodial" were sandwiched and optically coupled, in turn, between the photocathodes of tubes 1 and 2. Voltages were set to those which gave balance point operation. The additional count rate due to these discs in a 10 cm lead shield is given in Table IV. It is seen that quartz gives very little, if any, additional count rate and that "Pyrex", lime soda and "Kodial" give additional count rates which are not proportional to their potassium contents.

The spectrum of gamma radiation from 5 "Kodial" discs stacked on top of a 7.5 cm diam., 7.5 cm thick  $\text{NaI}(\text{Tl})$  crystal in a low background counter showed only a 1.46 MeV photopeak attributable to  $\text{K}^{40}$ . The photopeak count rate from the discs (total weight 56 g) was compared with that of an equivalent volume of  $\text{K}_2\text{SO}_4$  weighing 46.6 g and the  $\text{K}_2\text{O}$  content calculated to be 4.1%, which is in good agreement with the value quoted in Table IV.

As a check on the efficiency with which beta particles of maximum energy near that of  $K^{40}$  are detected, a source of  $P^{32}$  was deposited on nylon foil and sandwiched between the photocathodes and found to give an efficiency of approximately 30%. There is a larger proportion of high energy pulses from  $P^{32}$  beta

TABLE IV  
COINCIDENCE BACKGROUND FROM PHOTOCATHODE WINDOWS

Photocathode window	Additional count rate (cpm)		Quoted $K_2O$ content [15] (% by wt)	Calculated $\beta/\text{min}$
	Limited	Total		
Quartz (E. M. I.)	$0 \pm 2$	$0 \pm 2$	0	0
Lime-Soda (E. M. I.)	$30 \pm 2$	$34 \pm 2$	0.7	102
Lime-Soda (E. M. I.)	$35 \pm 2$	$40 \pm 2$	0.7	102
Lime-Soda (E. M. I.)	$29 \pm 2$	$34 \pm 2$	0.7	102
Lime-Soda (E. M. I.)	$26 \pm 2$	$30 \pm 2$	0.7	102
"Pyrex" (E. M. I.)	$35 \pm 2$	$37 \pm 3$	0.32	47
"Pyrex" (20th Cent)	$29 \pm 2$	$30 \pm 3$	0.32	47
"Kodial" (E. M. I.)	$68 \pm 2$	$71 \pm 3$	4.2	615
"Kodial" (E. M. I.)	$70 \pm 2$	$74 \pm 2$	4.2	615
"Kodial" (E. M. I.)	$66 \pm 2$	$71 \pm 3$	4.2	615
"Kodial" (E. M. I.)	$68 \pm 2$	$68 \pm 2$	4.2	615
2 "Pyrex" discs together	$60 \pm 3$	$61 \pm 3$	—	—

particles than from the radiation causing light in the window and this is probably due to the difference in mean beta energy.

It therefore appears likely that light from "Kodial" windows is largely attributable to  $K^{40}$  beta particles but that the contamination of "Pyrex" and lime soda windows is not all  $K^{40}$ .

#### 3.1.4. PHOTOMULTIPLIER BACKGROUND DUE TO EXTERNAL GAMMA AND COSMIC RADIATION

The proportion of the coincidence background attributable to external gamma and cosmic radiation was investigated using tubes 1 and 2 and shields of 10 cm Pb and a ring of Geiger Müller anti-coincidence counters\*. The photomultipliers were optically coupled and voltages were adjusted to give balance point operation. The results are summarized in Table V.

About  $20 \pm 2$  cpm are subtracted from the total counting rate by the anti-coincidence counters and if these are assumed to be near 100% efficient for the meson component, this is in approximate agreement with the known cosmic ray flux [16, 17].

The limited counting rate is only reduced by 7 (102-95) cpm when the anti-coincidence ring is used in addition to 10 cm Pb and the top discriminator, as 13 (143-123-7) cpm are due to pulses of amplitude greater than 50 V and are therefore already deleted by the top discriminators.

External radiation produces a much higher proportion of pulses over 50 V in amplitude than does any of the radioactivity in the photocathode windows.

The coincidence count rates with opaque materials between the photocathode windows and inside a 10 cm Pb shield are given in Table VI.

\* Type G 53 20th Century Electronics Ltd.



TABLE V  
PHOTOMULTIPLIER-COINCIDENCE BACKGROUND FROM EXTERNAL GAMMA  
AND COSMIC RADIATION

	Coincidence count rate (cpm)		Anti-coincidence count rate (cpm)	
	Limited	Total	Limited	Total
Unshielded	$130 \pm 1$	$185 \pm 2$	—	—
Inside 10 cm Pb	$102 \pm 0.5$	$143 \pm 0.5$	$95 \pm 0.4$	$123 \pm 1$

With the paper in position approximately seven (10-3) cpm are attributable to cosmic radiation. About 2 cpm are due to beta particles which penetrate the paper to give simultaneous light pulses in both photocathodes but these are stopped in the thick aluminium disc.

TABLE VI  
COINCIDENCE BACKGROUND WITH OPAQUE MATERIALS BETWEEN  
PHOTOCATHODE WINDOWS

	Coincidence count rate (cpm)		Anti-coincidence count rate (cpm)	
	Limited	Total	Limited	Total
Inside 10 cm Pb				
Black paper	$2.0 \pm 0.1$	$10.0 \pm 0.1$	$1.7 \pm 0.1$	$3.0 \pm 0.8$
0.02 mm Al	$1.8 \pm 0.2$	$10.4 \pm 0.2$	$1.5 \pm 0.2$	$3.1 \pm 0.2$
2.6 mm Al	$0.5 \pm 0.2$	$6.2 \pm 0.2$	$0.2 \pm 0.2$	$0.7 \pm 0.2$

### 3.1.5. SUMMARY OF ORIGINS OF PHOTOMULTIPLIER BACKGROUND

The contributions to background count rate from optically-coupled photomultipliers (1, 2) and (11, 12) are summarized in Table VII.

TABLE VII  
SUMMARY OF ORIGINS OF PHOTOMULTIPLIER BACKGROUND

Cause	Contribution to limited background count rate (cpm)	
	Tubes 1,2	Tubes 11,12
Soft radiation from laboratory contamination and cosmic radiation (absorbed in 10 cm Pb shield)	$28 \pm 2$	$22 \pm 2$
Radiation from contamination of lead shield (absorbed in 2.5 cm Hg shield)	$0 \pm 2$	$0 \pm 2$
Cosmic radiation not subtracted by top discriminator (deleted by anti-coincidence ring)	$7 \pm 1$	$6 \pm 2$
Window contamination	$70 \pm 4$	$0 \pm 2$
Contamination of counter materials, remaining external radiation and possibly tube operation	$25 \pm 5$	$24 \pm 3$

#### 4. Choice of photomultiplier

It is desirable from the point of view of simplicity and ease of operation, to have a counting system which will operate at room temperature. With recent developments in construction and processing, thermionic background in the so-called S-tubes has been so reduced that the random coincidence count rate at room temperature is negligible, while a high photocathode sensitivity has been maintained [18, 19].

Photocathode sensitivities of tubes suitable for tritium counting are generally in the range 30–60  $\mu\text{A/lm}$  but occasional tubes are produced with sensitivities approaching 80  $\mu\text{A/lm}$ . To check the importance of photocathode sensitivity on tritium counting efficiency, measurements were taken with the standard source for a number of photomultipliers of differing photocathode sensitivities and the results are shown in Table VIII. It is seen that the single channel efficiency does increase

TABLE VIII  
RELATIONSHIP BETWEEN PHOTOCATHODE SENSITIVITY AND MAXIMUM SINGLE CHANNEL EFFICIENCY

Tube No.	1	10	9	2	7	8	13	3	4	5	6
Photocathode sensitivity ( $\mu\text{A/lm}$ )	32	38	40	42	45	56	58	58	65	80	83
Max. single channel efficiency (%)	55	58	60	57	64	64	64	64	64	66	65

with increasing photocathode sensitivity but not linearly. The reason for the lack of correlation is probably that the number of single photon pulses is relatively small.

Backgrounds and efficiencies measured using the dioxane phosphor in container (b) and a number of photomultipliers are summarized in Table IX. It is apparent that,

TABLE IX  
COINCIDENCE EFFICIENCIES AND BACKGROUND COUNT RATES FOR VARIOUS PHOTOMULTIPLIERS IN CONTAINER (b) (110 ml)

Tubes	Limited efficiency (%)	Limited background in 10 cm Pb (cpm)			Figure of Merit (EVB- $\frac{1}{2}$ )
		Phosphor	Alcohol	Empty	
9514 S					
1, 2 ("Pyrex")	6.8	98 $\pm$ 2	71 $\pm$ 2	38 $\pm$ 2	15.1
3, 4 (Soda)	9.5	162 $\pm$ 3	151 $\pm$ 2	78 $\pm$ 2	16.5
5, 6 (Soda)	9.7	104 $\pm$ 3	72 $\pm$ 2	39 $\pm$ 2	20.9
7, 8 (Soda)	7.5	153 $\pm$ 3	145 $\pm$ 2	64 $\pm$ 2	13.3
6255 S					
9, 10 (Quartz)	6.3	41 $\pm$ 2	18 $\pm$ 2	11 $\pm$ 2	21.6
11, 12 (Quartz)	9.4	54 $\pm$ 2	31 $\pm$ 1	26 $\pm$ 1	28.1
13, 14 (Quartz)	5.3	56 $\pm$ 2	19 $\pm$ 2	13 $\pm$ 2	15.6

as expected, the coincidence efficiency increases with increasing photocathode sensitivity, and photomultipliers with quartz windows give the lowest background. The abnormally high background count rate of tubes 3, 4 and 7, 8 has been shown to be due to inadvertant use of windows having abnormally high potassium content in tubes 4 and 7.

The best tubes are, therefore, those with quartz windows and high sensitivity photocathodes.

Since both coincidence background and efficiency of a single photomultiplier system increase to a saturation value with increasing voltage, variation of the figure of merit with single tube efficiency was examined. The coincidence background count rate was measured as a function of single channel efficiency for tubes with optically-coupled windows, and applied voltages set to give the same single channel efficiency. The results plotted in Fig. 7 show that the relation between

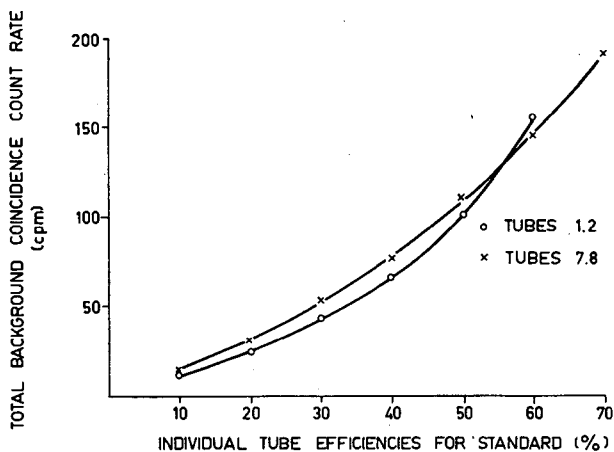


Fig. 7

Total background coincidence count rate  $\nu$ . single tube efficiency.

light interaction coincidence background and single channel efficiency is not linear. However, the coincidence efficiency is approximately equal to the square of the single channel efficiencies and, if the ratio of this to the square root of the background is taken, it can be seen that the figure of merit increases with increasing single channel efficiency, up to maximum single channel efficiency.

## 5. Design of phosphor container

The phosphor container was designed so that the photomultipliers were co-axial, as this arrangement is easy to operate within anti-coincidence counters and lead shields. Although it might be expected that the arrangement would be worse for light interaction background than one having the photomultiplier axes at right angles or parallel, the difference between the two systems would be small with a good reflector for maximum counting efficiency.

Suitable container materials are quartz (with a reflecting covering), PTFE, nylon, polished aluminium or stainless steel, or brass, plated with polished silver or nickel. The container may be sealed with quartz discs or the photomultiplier windows.

A comparison of container (b) and containers (d) and (e) with aluminium foil reflectors is made in Table X, and it is apparent that their performances are similar. Container (e) was selected for the final low background system to avoid possible contamination of the photocathode windows.

## 6. Design and performance of low background counter

In the final low background system, photomultipliers 11 and 12 were optically coupled to the 78 ml quartz container (e) with high viscosity silicone oil and the whole assembly was surrounded with 10 cm of lead. Filling, emptying and flushing were accomplished by gravity displacement from a brass header tank through 3 mm bore copper tubing. Circular coils in the brass tubing acted as complete light blocks.

TABLE X  
COINCIDENCE EFFICIENCIES AND BACKGROUND COUNT RATES FOR  
TUBES 11 AND 12 ON CONTAINERS (b), (d) AND (e)

Container Type	Vol. (ml)	Limited efficiency (%)	Limited background in 10 cm Pb (cpm)			Figure of merit, ( $EVB^{-\frac{1}{2}}$ )
			Phosphor	Alcohol	Empty	
(b)	110	9.4	$54 \pm 2$	$31 \pm 1$	$26 \pm 1$	28.1
(b)	250	4.1	$76 \pm 2$	$32 \pm 2$	$16 \pm 2$	23.5
(d)	215	7.1	$113 \pm 3$	$68 \pm 2$	$38 \pm 2$	28.7
(e)	78	13.9	$61 \pm 2$	$44 \pm 2$	$36 \pm 1$	27.8

One flushing with dioxane removed all but 0.1% of the previous solution and after a further flushing there was no detectable contamination.

This system gave a limited coincidence efficiency of 13.9% for 16 ml of water in 62 ml of dioxane containing 6 g/l of PPO and 100 g/l of naphthalene, with a limited coincidence background of 61 cpm.

If the minimum detectable specific activity (*M.D.A.*) is defined as that which gives, in a time *t* min, a count having a relative standard deviation of 0.5 [4], then it can be shown that

$$M.D.A. = \frac{9 \times 10^{-5}}{EV} \sqrt{\frac{B}{t}} \mu\text{c/ml} \quad (2)$$

for a system counting *V* ml. of sample with an efficiency of *E*% and having a constant known background, *B* cpm.

With the above system, the minimum detectable specific activity with a counting time of 30 min is  $6 \times 10^{-7} \mu\text{c/ml}$ .

Some improvement in this figure will be obtained when photomultipliers with quartz windows become available with photocathode sensitivities higher than those used. Improvement may also result from further selection in shielding materials. The container volume was based on previous work [4] and the optimum will be found by measurements on containers of different volumes, but this is not expected to improve the sensitivity significantly.

## ACKNOWLEDGEMENTS

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# RECENT ADVANCES IN LOW-LEVEL SCINTILLATION COUNTING OF TRITIUM

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Abstract — Résumé — Аннотация — Resumen

**Recent advances in low-level scintillation counting of tritium.** Studies have been made of the liquid scintillation counting system with the objective of optimizing detection sensitivity as expressed by a function of sample volume, efficiency and background. The investigation included a review of scintillator composition. A dioxane-naphthalene-water system having a water content of 18.6% was selected as the most satisfactory composition. Further studies of counting cell geometry and scintillator volume have led to the use of a cylindrical container of "Teflon" with high gain quartz face photomultipliers in direct contact with the solution. This system gave a tritium detection sensitivity corresponding to a concentration of  $0.55 \times 10^{-12}$  c/ml at an efficiency of 6.9% and a background of 52 cpm. A water sample volume of 31.6 ml was used with total scintillator volume of 170 ml.

An internal  $\text{Co}^{57}$  source was found to be a suitable monitor of tritium-counting efficiency in the range 2 to 7% with a standard deviation of 0.1%. It has the advantage over previous methods in that it provided a rapid efficiency determination without modification of the sample.

Studies of background reduction were made to evaluate the contribution of luminous interaction and cosmic radiation. A plastic envelope anticoincidence shield was used in the study. Long term effects on stability of the system caused by sample deterioration and counting equipment drifts were evaluated.

**Progrès récents dans le comptage à scintillations de faibles teneurs en tritium.** Les auteurs ont étudié un dispositif de comptage à scintillateur liquide, en vue de rendre optimum la sensibilité de la détection, définie en fonction du volume de l'échantillon, du rendement de comptage et du bruit de fond. Les recherches ont porté notamment sur la composition du scintillateur. On a choisi un mélange dioxane-naphtalène-eau, dans lequel cette dernière entrait pour 18,6%, parce que sa composition s'est révélée la plus satisfaisante. D'autres études, qui portaient sur la géométrie de la cellule de comptage et le volume du scintillateur, ont amené les auteurs à utiliser un récipient cylindrique en «Teflon» et des photomultiplicateurs à fenêtre en quartz à gain élevé, en contact direct avec la solution. Ce dispositif permet d'obtenir une sensibilité de détection correspondant à une concentration en tritium de  $0,55 \cdot 10^{-12}$  c/ml, avec un rendement de 6,9% et un bruit de fond de 52 cpm. Les auteurs ont utilisé un échantillon d'eau de 31,6 ml, le volume total du scintillateur étant de 170 ml.

Les auteurs ont constaté qu'une source interne de cobalt-57 permettait de contrôler efficacement le rendement du comptage du tritium, dans la gamme allant de 2 à 7%, avec un écart type de 0,1%. Par rapport aux méthodes plus anciennes, ce procédé offre l'avantage de permettre une détermination rapide du rendement sans modifier l'échantillon.

Les auteurs ont étudié la réduction du bruit de fond, pour évaluer la part de l'interaction lumineuse et celle des rayons cosmiques; ils ont utilisé à cette fin une protection d'anticoincidence, à enveloppe en matière plastique. Ils ont évalué dans quelle mesure la détérioration des échantillons et les dérives du matériel de comptage tendent à réduire, à longue échéance, la stabilité du dispositif.

**Последние достижения в области сцинтилляционного счета трития низкого уровня.** Было проведено исследование жидкостной сцинтилляционной счетной системы с целью оптимизировать чувствительность регистрации, выражаемую функцией величины образца, эффективности и фона. Исследование включало пересмотр состава сцинтиллятора. Наиболее удовлетворительным был найден состав в системе диоксана-нафталиновода с содержанием воды в 18,6%. Даль-

нейшее изучение геометрии счетного сосуда и объема сцинтиллятора привело к использованию цилиндрического контейнера из тефлона с фотоумножителями с высокоусиленной кварцевой поверхностью в непосредственном контакте с раствором. Эта система показала чувствительность регистрации трития, соответствующую концентрации  $0,55 \times 10^{-12}$  кюри/миллилитр при эффективности в 6,9% и фоне в 52 отсчета в минуту. Был использован образец с объемом воды в 31,6 миллилитра при общем объеме сцинтиллятора в 170 миллилитров.

Было обнаружено, что внутренний источник кобальта-57 достаточно хорошо контролирует эффективность счета трития в пределах от 2 до 7% со стандартным отклонением в 0,1%. По сравнению с предыдущими методами этот способ имеет то преимущество, что позволяет быстро определить эффективность без изменения образца.

Для оценки значения люминисцентного взаимодействия и космической радиации было исследовано уменьшение фона. При этом был использован с пластиковой оболочкой экран антисовпадения. Было также изучено долгосрочное влияние износа образца и дрейфа счетного оборудования на стабильность системы.

**Progresos recientes en el recuento por centelleo de bajas concentraciones de tritio.** Se han llevado a cabo estudios sobre el sistema de recuento por centelleo de líquidos con objeto de establecer las condiciones óptimas de sensibilidad para la detección, expresadas en función del volumen de la muestra, del rendimiento de recuento y de la actividad de fondo. Estas investigaciones comprendieron un estudio de la composición del centelleador. Se ha elegido como composición más satisfactoria una mezcla de dioxano-naftaleno-agua, esta última en la proporción de 18,6%. Los nuevos estudios realizados acerca de la geometría de la celda de recuento y el volumen del centelleador han conducido al empleo de un recipiente cilíndrico de "Teflon" con fotomultiplicadores de elevada ganancia, dotados de una ventana de cuarzo, en contacto directo con la solución. Con este sistema se ha logrado una sensibilidad de detección correspondiente a una concentración de tritio de  $0,55 \times 10^{-12}$  c/ml con un rendimiento de 6,9% y un fondo de 52 imp/min. Se utilizó una muestra de agua de 31,6 ml y un centelleador de 170 ml de volumen total.

Se ha podido comprobar que una fuente interna de  $^{57}\text{Co}$  constituye un medio adecuado para controlar el rendimiento de recuento del tritio en el intervalo comprendido entre 2 y 7%, con una desviación standard de 0,1%. Respecto de los métodos anteriores, posee la ventaja de que permite una rápida valoración del rendimiento sin necesidad de modificar la muestra.

Se efectuaron estudios sobre la reducción del fondo con miras a evaluar la influencia de la interacción luminosa y de las radiaciones cósmicas. En el estudio se empleó un blindaje de anticoincidencia con una envoltura de material plástico. Se determinaron los efectos a largo plazo ejercidos sobre la estabilidad del sistema por la deterioración de las muestras y las desviaciones en el equipo de recuento.

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## Introduction

In tracer applications it is often important to reduce the amount of a radioisotope to a minimum commensurate with the accuracy required to meet a research objective, but with due regard for hazard and economy. These considerations have arisen repeatedly in the employment of tritiated water in large-scale hydrologic studies.

In the comparison of various measurement systems, it is desirable to employ a sensitivity criterion that includes the major determining parameters and gives a statistically meaningful measure of individual merit. Several indices of merit have been used, the most common being the square of instrument efficiency divided by background. A more explicit merit is the concentration sensitivity [1] or minimum detectable concentration of radioactivity [2]. The statistical confidence limits selected to delineate "detectability" are quite arbitrary, but the use of a 95% limit



is becoming widely accepted and was used to compute concentration limits of detectability throughout this investigation. By setting the net sample counting rate equal to two standard deviations of the Poisson distribution describing the theoretical detection error, an expression may be developed for the minimum detectable activity concentration [2]:

minimum detectable activity concentration ( $\mu\text{Ci/ml}$ )

$$= \frac{9.0 \times 10^{-5}}{Ev} \sqrt{\frac{n_b}{t}}, \quad (1)$$

in which  $E$  is the efficiency, in per cent;  $v$ , the sample volume, in ml;  $n_b$ , the background, in counts/min; and  $t$ , the counting time, in min. The reciprocal of equation (1), with a counting time of 30 min, has been designated "detection sensitivity" and is given by equation (2):

$$\text{detection sensitivity (l/}\mu\text{Ci)} = 61 \frac{Ev}{\sqrt{n_b}}. \quad (2)$$

The detection sensitivity corresponds to the reciprocal of the concentration of a radioisotope which, if a sample of volume  $v$  were counted for 30 min, would have a probability of 0.975 of providing a counting rate greater than background. It should be kept in mind that the coefficient of variation of a measurement made at the minimum detectable activity concentration is 50%, a rather appreciable error for many applications. Furthermore, equation (2) defines a theoretical sensitivity that is only achieved in practice by very stable instrument operation.

The general objective of this investigation was to maximize the detection sensitivity of the liquid scintillation spectrometer. The investigation was largely limited to tritiated water measurements. By optimizing the scintillator composition and by increasing the volume of scintillator placed between the photomultiplier tubes, it was possible to increase greatly the volume of sample counted with only a relatively small reduction in efficiency, but with a great increase in the  $Ev$  product. Such an approach is, of course, only permissible in instances where sample volumes are not limited to a few ml.

The study employed two Packard Tri-Carb liquid scintillation counters, one equipped with DuMont 6292 photomultipliers, the other with E.M.I. 6255 A quartz-faced photomultipliers. Both instruments were modified to receive counting cells of various shapes and sizes. In order to accommodate the E.M.I. tubes to the standard Packard counter, it was necessary to modify the photomultiplier sockets and to introduce an external attenuator between the analyser preamplifier and its amplifier. Except as otherwise noted, each scintillator and cell geometry were examined at photomultiplier high voltages, amplifier gains, and discriminator settings providing a maximum ratio of signal to the square root of background, these conditions comprising balance-point operation as suggested by ARNOLD [3]. In most instances measurements were made in the 10–90 V channel.

### Optimization of scintillator composition

Studies of scintillator composition were carried out with the DuMont photomultiplier-equipped spectrometer and 20 ml commercial counting vials. Preliminary comparisons of several scintillators clearly demonstrated the merit of 1–4 dioxane as the solvent, since it is miscible with water in all proportions and thus permitted wide variations in water content. By using a commercial dioxane containing 4.0 g/l PPO (2,5-diphenyloxazole) and 0.1 g/l  $\alpha$ -NPO (2-[1-naphthyl]-5-phenyloxazole),

to which were added various amounts of water and naphthalene, it was possible to determine the composition providing a maximum value of eV and thus a maximum sensitivity. A typical series of such measurements is shown in Fig. 1 for a naphtha-

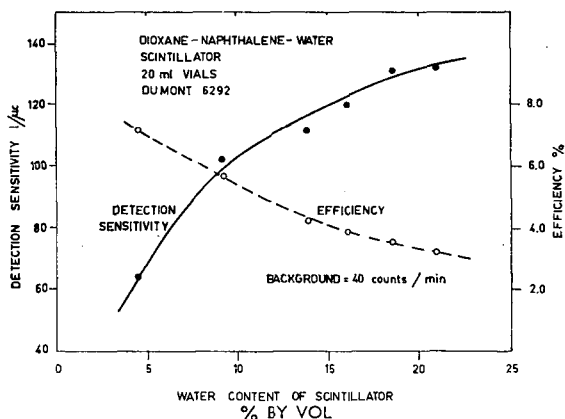


Fig. 1

Influence of scintillator composition on detection sensitivity and efficiency.

lene concentration of 100 g/l of dioxane. Higher concentrations of naphthalene brought about only minor improvements in efficiency, and consequently 100 g/l was employed in all subsequent measurements. Fig. 1 clearly demonstrates that maximum sensitivity does not necessarily result from a scintillator composition providing the highest level of efficiency.

A further investigation of the dioxane-naphthalene-water system led to the selection of PPO and POPOP (1,4-di[2-(5-phenyloxazolyl)]benzene) at 6.0 and 0.3 g/l of dioxane, respectively, as providing the greatest sensitivity. The scintillator solutions prepared for counting were composed of water (18.6% by volume) and the dioxane solution of naphthalene and the two phosphors (81.4%). The function of POPOP, often termed a secondary phosphor, was to shift the light emission spectrum of the scintillator into the visible range and more nearly to match the spectral range of maximum response of the DuMont photomultipliers. The E.M.I. tubes, having an S13 type photocathode sensitive in the ultraviolet region, were found to perform equally well with a scintillator containing little or no POPOP.

In comparing two lots of commercial dioxane, the presence of impurities was observed to result in an 18.4% difference in counting efficiencies as determined with 20 ml vials. A second comparison of scintillator solutions prepared with the two lots of dioxane is shown in Fig. 2. In this instance, employing a polished aluminium counting cell, performance of the second lot of dioxane proved superior to that of the first lot by a factor of two. Distillation of both lots of dioxane with iron, and in a nitrogen atmosphere for the removal of peroxides, resulted in only a small improvement in counting efficiency.

It was evident from this study that improvements in sensitivity brought about by variations in scintillator composition were in no sense absolute, but were dependent on the geometric relation of scintillator to photomultiplier. Unless otherwise noted, all data reported herein were obtained with the more satisfactory dioxane.

### Relation of counting cell geometry to sensitivity

A comparison was made of the detection sensitivity obtainable with various counting cells employing the dioxane-naphthalene-water scintillator previously described. The cells included the commercial 20 ml and 60 ml Crystal Lite vials and specially-constructed 60 ml quartz and 140 ml "Pyrex" vials. These four vials were cylindrical in shape with their axes normal to that of the photomultipliers.

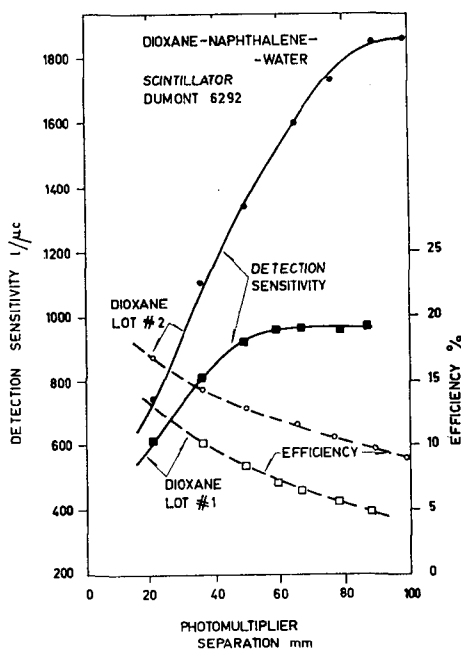


Fig. 2

Effect of photomultiplier separation and dioxane on detection sensitivity and efficiency.

Three cylindrical vials were also used mounted coaxially with the photomultipliers and having end plates parallel to the photomultiplier face plates. The latter three cells were examined with and without a silicone optical couple. The results of efficiency and background measurements on the seven cells are shown in Table I, together with the calculated detection sensitivities. The advantage achieved by using large optically-coupled co-axial cylindrical cells is evident. The major disadvantage of such cells is their greater cost and the inconvenience of work with a cell wetted by the coupling fluid.

The attributes of the cylindrical geometry were investigated further with the DuMont photomultipliers connected with a polished aluminium sleeve, allowing separation distance ranging from 20 to 100 mm and permitting the scintillation to be in direct contact with the photomultiplier face plates. Detection sensitivity and efficiency for scintillators prepared with the two lots of dioxane have been plotted against photomultiplier separation in Fig. 2. Background decreased from about 125 counts/min at 25 mm separation to 105 counts/min at 90 to 100 mm separation. As observed earlier, maximum sensitivities were recorded at appreciably less than maximum efficiencies. However, it was evident that as the volume of scintillator was

increased, the detection sensitivity must pass through a maximum and then decrease. With the two-photomultiplier coincidence system a sufficient number of photons must reach the photocathodes to produce at least one photoelectron at each. Since only 30 to 40 photons are produced by a tritium beta of average energy, and the conversion efficiency at each photocathode is perhaps only 10%, it is evident that

TABLE I  
CHARACTERISTICS AND PERFORMANCE OF VARIOUS COUNTING CELLS

Cell	Background $n_b$ (counts/min)	Efficiency E (%)	Detection sensitivity $61 \text{ eV}/\sqrt{n_b}$ ( $1/\mu\text{c}$ )
20 ml, Crystal Lite	49	5.01	160
60 ml, Crystal Lite	49	2.17	210
60 ml, quartz	49	2.61	260
140 ml, "Pyrex"	112	2.00	300
180 ml, "Vycor" (aluminium foil covered)*	291 (348)	3.43 (7.61)	410 (840)
180 ml, "Pyrex" (silvered)*	168 (242)	3.16 (7.95)	500 (1020)
87 ml, quartz*	60 (103)	4.10 (7.04)	530 (680)

\* Cylindrical cell mounted co-axially with respect to photomultipliers. Values in parentheses were determined with an optical coupling. Water content of scintillator was 18.6% of the nominal cell volume [5].

changes in cell geometry, or reductions in reflectivity of the cell surfaces and transmissibility of the scintillator, may seriously impair counting efficiency. In a long cylindrical cell, a release of photons near one photomultiplier might well be undetected by the more distant photomultiplier. From these studies it became apparent that with present photomultipliers little could be achieved by enlarging counting cells beyond photomultiplier separations of 100 mm. In a majority of the subsequent measurements, separations of 70 to 80 mm were employed as practical upper limits.

In order to utilize the instrument for low-level measurements and less sensitive, but more convenient, measurements with 20 ml vials, an insert cell was constructed of silvered brass. The cell, which could be readily introduced into the cavity between the photomultipliers, had a volume of 170 ml and was bounded at the ends by the photomultiplier face plates. This arrangement gave an efficiency of 6.34%, a background of 100 counts/min, and a detection sensitivity of 1220  $1/\mu\text{c}$ . Sixteen background measurements over a four-day period gave a variance as expected from the Poisson distribution. The operating temperature was 3 °C. Experience has shown that care should be exercised in selecting the materials of the insert cell to avoid internal contamination. A second silvered insert cell gave a background 10% greater than the first.

#### Comparison of Dumont 6292 and E.M.I. 6255 A photomultiplier tubes

There are several potential advantages of the E.M.I. 6255 A photomultipliers for low-level tritium counting. The quartz face-plate allows the shorter wave lengths ( $< 4000 \text{ \AA}$ ) of the PPO emission spectrum to reach the photocathode, potentially removing the desirability of employing secondary phosphors such as  $\alpha$ -NPO or

POPOP. Undoubtedly, some loss occurs in the additional energy transfer from primary to secondary phosphor. Another advantage of the quartz face-plate is the elimination of  $K^{40}$  present in most glasses and believed to be a significant contributor to background under the circumstances of tritium measurements.

A comparison of the two photomultipliers was carried out with the silvered insert cell and the dioxane-naphthalene-water scintillator containing both PPO and POPOP. The E.M.I.-equipped instrument gave an efficiency of 6.90%, a background of only 57 counts/min, and a detection sensitivity of 1680 l/ $\mu$ c, a significant improvement over the 1220 value determined for the DuMont photomultipliers. The lesser background of the E.M.I. tubes is of particular interest. In addition, the higher gain of these tubes provided better discrimination against external noise.

Additional studies of the E.M.I. photomultipliers were carried out to determine the merit of employing POPOP and the relative reflectivities of polished silver, representing a specular reflector, and "Teflon", a diffuse reflector. POPOP concentrations of 0.0, 0.1, and 0.2 g/l exhibited no significant influence on counting efficiency. However, "Teflon" was clearly a more effective reflector than silver, giving an efficiency of 7.15% with a background of 57 counts/min, and a detection sensitivity of 1860 l/ $\mu$ c. Under similar circumstances the silver cell presented an efficiency of 5.28%, a background of 51 counts/min, and a detection sensitivity of 1420 l/ $\mu$ c. "Teflon" was particularly sensitive to photoexcitation by fluorescent lights and daylight, with subsequent phosphorescent emissions persisting, even in coincident operation, for extended periods. By minimizing exposure of the "Teflon" cell to light while changing samples, the contribution to background was reduced to less than 1 count/min.

#### Cobalt-57 as an internal standard

One of the factors limiting the true tritium detection sensitivity is variation in counting efficiency caused by small concentrations of quenching impurities carried into the scintillator by the sample. The most common technique for ascertaining quenching effects and measuring counting efficiencies is to introduce a small amount of a standard tritium solution into the scintillator and to make a second measurement of the counting rate. This so-called "internal standard" method has the disadvantage of modifying and contaminating the scintillator.

In search for a suitable efficiency monitor that would be free from these disadvantages, the use of  $Co^{57}$  as an internal solid source was investigated.  $Co^{57}$  decays by electron-capture with a 270 d half-life and with two predominant gamma photons in cascade:  $\gamma_1 = 14$  keV and  $\gamma_2 = 122$  keV with  $\gamma_1$  undergoing a high degree of internal conversion ( $e/\gamma = 15$ ) [4]. It was anticipated that with the two channel scintillation counter, the internally converted  $\gamma_1$ , would be counted predominantly in the lower channel, while  $\gamma_2$  would register mainly in the upper channel, the exact channel count ratio depending on efficiency. This ratio could be an effective monitor of tritium counting efficiency, provided a definite correlation between the two variables could be shown that would be reproducible and independent of the cause of efficiency change.

Several measurements were made to test the validity of these assumptions. The  $Co^{57}$  source was deposited at the tip of a two inch long platinum wire. The active area was then covered with 20  $\mu$ g/cm<sup>2</sup> gold in order to prevent contamination of the solution which occurred in the preliminary experiments [5]. The experiment consisted of measurement of the high-to-low channel count ratio due to  $Co^{57}$  with the platinum wire in the centre of the scintillator volume, for different scintillators,

photomultipliers and quenching conditions. Three typical curves are shown in Fig. 3. Long-term operation indicates that tritium counting efficiency can be determined within 0.1% [5], which is satisfactory for most applications.

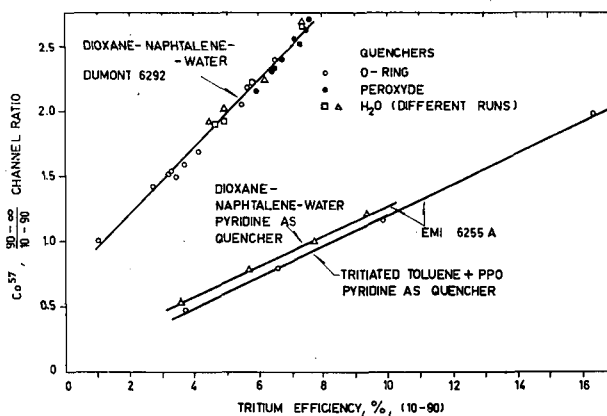


Fig. 3

Relation of  $\text{Co}^{57}$  channel ratio to tritium counting efficiency.

### Origin and composition of background

Although background influences detection sensitivity only as its square root, it remains an important consideration in a low-level tritium counting system and merits more detailed investigation. The knowledge of the origin of the various components of background and their quantitative estimate are prerequisites to a rational approach to background reduction. Several authors including SWANK, ARNOLD and AUDRIC [6] have examined the nature of background in scintillation counting, but the particular origin of the major contributors remained uncertain.

The following sources of background were considered as potential contributors to the actually measured background and their contributions were analysed or estimated.

#### 1. EXTERNAL GAMMA RADIATION

It originates with the natural radioactive emitters in the air and the surrounding structures, fission products in the environment and various radioisotopes in neighbouring laboratories.

#### 2. COSMIC RADIATION

Charged particles and neutrons should be considered.

#### 3. INTERNAL RADIOACTIVE CONTAMINATION

Alpha, beta and gamma emitters incorporated in the shield, insert cell, photomultipliers and possibly scintillator.

#### 4. RANDOM COINCIDENCES AND LIGHT INTERACTION

And other, mainly count rate, dependent contributions.

Amplifier noise, electromagnetic disturbances and other sources of background of non-statistical nature were virtually eliminated and were not considered here.

In order to separate better the contributions of the various components of background a special lead and stainless steel shield was constructed, that had a semi-annular cavity. A properly-shaped plastic scintillator sheet, 5/8 in thick and 8 in  $\times$  12 in in size was inserted into this cavity and a photomultiplier with a light guide was attached to it. The output of the photomultiplier was fed into an anti-coincidence circuit. The pulses appearing in the low channel (10—90 V) or the high channel ( $>90$  V) could be placed alternately in anti-coincidence with the pulses of the plastic scintillator shield. In this manner pulses resulting from interaction of cosmic radiation with the scintillator and with the photomultiplier glass could be accounted for.

Background measurements were made using the normal scintillator solution at different photomultiplier separations, in order to indicate the volume dependence of the background. Similar measurements were performed with ethanol and air instead of the scintillator solution. Ethanol, being a poor scintillator [7], should not show the volume effects but would ensure optical coupling conditions for pulses originating in the glass of the photomultipliers. The results of these measurements are given in Table II and served as a basis for the following estimate of the various components of background.

TABLE II

## BACKGROUND ANALYSIS AND REDUCTION WITH ANTI-COINCIDENCE SHIELD

Photomultiplier Separation	73 mm		31 mm		15 mm	
	Coin.*	Anti-coin.**	Coin.	Anticoin.	Coin.	Anticoin.
10-90 V						
Air	16.4	12.0	21.2	18.0	23.3	18.5
Ethanol	21.6	18.2	26.1	23.0	29.9	26.0
Scintillator	55.6	48.0	42.5	38.1	42.0	37.2
90-00 V						
Air	50.8	19.4	46.8	18.8	40.8	17.1
Ethanol	82.5	41.9	65.6	35.3	58.6	28.8
Scintillator	342	286	290	204	177	137

\* Tri-Carb., coincidence operation

\*\* Tranco, anticoincidence operation

Theoretical standard deviation of all measurements in 10-90 channel less than 1 counts/min

## External gamma radiation

An estimate of the gamma contribution to background was made by observing the influence of an external gamma source on the two channels of the liquid scintillation counter and on an independent NaI detector. From this experiment the gamma radiation appearing in the 10—90 channel was estimated to be no greater than 4 counts/min. The corresponding external gamma background of the 90— $\infty$  channel was approximately 20 counts/min.

## Cosmic radiation

The contribution of the charged particle component of cosmic radiation was expected to appear in coincidence with the plastic shield and therefore could be

readily accounted for. At a photomultiplier separation of 73 mm the difference between the scintillator data in coincidence and in anti-coincidence was 7.6 counts/min. It is probable that some small portion of this value may be attributed to external gamma radiation undergoing Compton scatter with the liquid scintillator with a subsequent interaction with the plastic scintillator. It may therefore be stated that 7.6 counts/min represents the maximum cosmic radiation contribution. The neutron component was estimated from the known flux and scintillation cross-sections to range between 0.05 and 0.20 counts/min, i. e. appreciably less than one count/min.

### Internal radioactive contamination

The main contribution from this source was  $K^{40}$  in the photomultiplier face plates as previously shown by the introduction of the quartz-faced photomultipliers. The reduction in background was from 100 to about 57 counts/min. However, not all sources of internal contamination were removed and those believed to remain are listed below.

- (1) The remaining  $K^{40}$  in the envelope of the E.M.I. photomultipliers may contribute about 1.6 beta/min and 0.18 gamma/min g of glass [8].
- (2) Quartz may contribute up to 15 cpm alpha in the photomultiplier face-plates [9].
- (3) Aluminium contains  $0.3 \mu\mu\text{c Ra/g}$  contributing 4.6 gamma/min g [8].
- (4) The stainless steel and lead were of recent origin and undoubtedly contained considerable activity.

A comparison of the ethanol and scintillator data in Table II indicates that the volume dependent background was greater than 30 counts/min in the low channel and about 250 counts/min in the high channel. The special shield was apparently constructed of contaminated materials which contributed about half of these values. The ethanol residual of 18 counts/min in the low channel included some contribution from the remaining  $K^{40}$  causing Cerenkov radiation in the face plates and glass envelope.

### Random coincidence and light interaction

The random coincidence rate can be accounted for if the resolving time is known. It is given by the expression  $2 \tau n_A n_M$ , where  $\tau$  is the coincidence resolving time and  $n_A$  and  $n_M$  are the analyser and monitor photomultiplier counting rates, respectively. However, several investigators have suggested that light interaction between photomultipliers, often termed the "light-dark current", is responsible for a large part of the coincidence background. If we assume this to be caused by light or ion feedback to the photocathode, the effect would be dependent on the individual photomultiplier counting rates. The total background,  $n_b$ , would then have two single photomultiplier counting rate dependent components and could be described by the expression

$$n_b = n_i + k(n_A + n_M) + 2 \tau (n_A \times n_M), \quad (3)$$

where  $n_i$  is the rate independent component and  $k$  is the interaction coefficient, assumed equal for both photomultipliers in order to simplify the analysis.

This expression was tested experimentally by changing the temperature of the photomultipliers and consequently changing the rate of thermionic emission with the results shown in Fig. 4. The tests were performed at two different voltage and bias



settings and the resulting lines of best fit corresponded to a coincidence resolving time of about  $0.30 \mu\text{s}$  and an interaction coefficient estimated by a regression analysis to be less than  $10^{-5}$ . The linearity of the lines shown on Fig. 4 infer that the term  $2\tau n_A n_M$  fully accounts for the increase in background with increasing photomultiplier temperature. Under these circumstances, and with  $n_A = n_M = 10\,000$  counts/min, light interaction would contribute less than 0.2 counts/min.

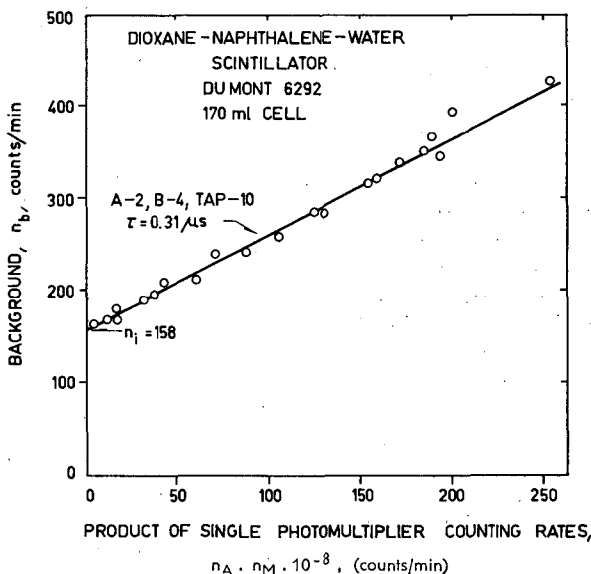


Fig. 4

Background dependence on single photomultiplier counting rates.

Objections can be raised to the above procedure on the grounds that only thermionic emission was varied and that other components of dark current appear to predominate at low temperatures [10]. If the light interaction originates with such reactions as electrical discharge or electroluminescence, it would not be expected to be single counting rate dependent and would appear as some part of  $n_i$ . A different approach to this investigation is described by BOYCE and CAMERON [11].

### Summary of background analysis

Based on the above results and analyses, the 56 counts/min background may be apportioned among its various contributors approximately as follows.

External gamma radiation	4 counts/min
Cosmic radiation	7 counts/min
Internal gamma contamination	30 counts/min
Random coincidences	1 counts/min
Cerenkov radiation and non-rate dependent light interactions (if existent)	14 counts/min
Total	56 counts/min

In the normally employed shield the background was only 43 counts/min, the difference of 16 counts/min being due to the lower internal contamination.

## Summary and Conclusion

The foregoing investigations of the optimization of low-level tritium measurement has made possible a maximum detection sensitivity of 1860 l/ $\mu$ c or, expressed as a minimum detectable tritium concentration, 0.54  $\mu$ c/ml. The optimization of scintillator composition and counting geometry, including a direct optical couple of scintillator to photomultiplier, are in large part responsible for the improved sensitivity. The use of high gain and high efficiency quartz-faced photomultipliers also improved the sample to background ratio, mainly through background reduction. The use of a  $\text{Co}^{57}$ -efficiency monitor increased the accuracy of the measurements by accounting for efficiency variations.

Recent developments in related fields indicate, however, that significant advances are still possible. New isotope exchange techniques allow the use of larger effective sample volumes and better scintillator composition [12]. The foregoing background analysis indicates that the use of carefully-selected cell and shield materials should result in a major reduction in background. Larger-diameter, radioactivity-free photomultipliers are being produced [13] and these will allow the use of larger sample volumes, without a corresponding increase in background. These considerations indicate that detection sensitivities of over 20 000 l/ $\mu$ c may be expected, making the liquid scintillation method at least equivalent to all other known techniques of low-level tritium measurement.

## ACKNOWLEDGEMENTS

This investigation was conducted at the Sanitary Engineering Research Laboratory of the University of California, Berkeley, under contract with the United States Atomic Energy Commission and Region 2, United States Bureau of Reclamation. The authors are indebted to Dr. Joseph A. Lieberman of the Atomic Energy Commission and Mr. Earl H. Bradley of the Bureau of Reclamation for their assistance and support in the conduct of these studies.

The authors like also to thank Dr. J. F. Cameron, Dr. M. Anbar and Dr. A. Heller for the advance information on their unpublished results.

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## DISCUSSION XVI

**W. F. Libby** (United States of America): Could Mr. Nir indicate lowest tritium concentration in tritium units.

**A. Nir** (Israel): I must apologize for not presenting the results in tritium units at this meeting. In the present case, the figure is about 100 T.U. The predicted figure is about 10, but we believe it will be better than that. These estimates are, of course, based on an assumed counting time of 30 min.

**F. Begemann** (Federal Republic of Germany): Incidentally, this agrees exactly with the figures in the paper by Boyce and Cameron (p. 231). I have just made a calculation on the basis of their experimental set-up and the result is 100 T.U.

**B. Gordon** (United States of America): I am puzzled as to the reasons for using a cobalt-57 instead of a liquid internal standard. While the use of the cobalt needle is a rather elegant technique, it involves additional work owing to the need to recover the water sample, which is not the case with a high-boiling internal standard.

In a laboratory where there were many samples to count, a large number of needles would have to be prepared for use in an automatic sample changer and this would be a disadvantage. I therefore feel that the cobalt needle is an interesting but not an essential modification.

**A. Nir**: I admit that the cobalt needle method is probably not adapted to an automatic counting procedure. I do not yet know whether it can be so adapted. As far as the non-automatic procedure is concerned, an efficiency estimate with the cobalt needle takes about 2 min. This is the counting time required for obtaining the statistics which form the basis of the results we have obtained.

**K. H. Kimbel** (Federal Republic of Germany): It may perhaps be of interest to point out that the use of polyethylene instead of glass containers for single phototube liquid scintillation counting of sulphur-35, carbon-14 and tritium may reduce the background count by about 50% and increase counting efficiency to a considerable extent. I think that the reduction may be due to the low potassium content, the low fluorescence and the reflector action of this semi-transparent plastic material. A further advantage is that the containers are inexpensive and can be discarded after use.



# PHOSPHORESCENCE IN LIQUID SCINTILLATION COUNTING

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Abstract — Résumé — Аннотация — Resumen

**Phosphorescence in liquid scintillation counting.** Phosphorescence is a phenomenon which is undesirable in liquid scintillation counting, especially at low levels and with single channel apparatus. The phosphorescence has been studied of materials which are likely to be incorporated in a scintillation counting system. The effect of time of excitation and the variation with overall detection efficiency has been investigated. Some selected liquids of very high purity have also been included. An analysis of the decay curves has been made, and the results evaluated in terms of a practical counting system.

**La phosphorescence dans le comptage à scintillations des liquides.** La phosphorescence est un phénomène à éviter dans le comptage à scintillations des liquides, notamment pour la détection des faibles activités et pour les appareils à un seul canal. Les auteurs ont étudié la phosphorescence de certains matériaux qui peuvent être incorporés dans les dispositifs de comptage à scintillations. L'effet du temps d'excitation et les variations en fonction du rendement global de détection ont fait l'objet de recherches. Les auteurs étudient aussi certains liquides choisis, de très grande pureté. Ils ont analysé les courbes de désintégration et évalué les résultats sous l'aspect de la mise au point d'un dispositif de comptage pratique.

**Фосфоресценция в жидкостных сцинтилляционных счетчиках.** Фосфоресценция является нежелательным явлением в жидкостных сцинтилляционных счетчиках, особенно при низких уровнях радиоактивности и с применением одноканальных приборов. Была изучена фосфоресценция материалов, которые могут быть включены в систему счета сцинтилляций. Были исследованы эффект времени возбуждения и колебания в общей эффективности обнаружения. Были включены некоторые отдельные жидкости очень высокой чистоты. Был проведен анализ кривой распада, и результаты подсчитаны в единицах практической счетной системы.

**La fosforescencia en el recuento mediante centelleadores líquidos.** La fosforescencia constituye un fenómeno que conviene evitar en el recuento mediante centelleadores líquidos, especialmente si las actividades son bajas y si se trabaja con aparatos de canal único. Los autores han estudiado la fosforescencia de algunos materiales susceptibles de incorporarse a los sistemas de recuento por centelleo. Investigaron el efecto del tiempo de excitación y las variaciones en función del rendimiento global de detección. El estudio comprendió también algunos líquidos escogidos de pureza muy elevada. Los autores efectuaron asimismo un análisis de las curvas de desintegración y evaluaron los resultados obtenidos con referencia a un sistema de recuento práctico.

## Introduction

Some substances when exposed to light are able to absorb energy and store this for a time before releasing it again as radiation. The process is covered by the general term luminescence and most frequently observed as fluorescence, in which the lifetime of the excited state is short, usually less than 1  $\mu$ sec; the term

phosphorescence is used when the mean lifetime is appreciably greater than this although no definition on the basis of lifetime or mechanism of the process would be universally acceptable.

Phosphorescence in the solid state is well known and has been the subject of considerable research, general theories having been set out by GARLICK [1]. Reports of phosphorescence from substances in the liquid state at room temperature were rare before high-sensitivity photon counting equipment was developed for liquid scintillation counting. Complex organic molecules have been the subject of considerable investigation by workers interested in luminescence although for observation of phosphorescence by the techniques usually employed it has been necessary to reduce radiationless deactivation of the excited states by working in solutions cooled to about 90 °K or in solid glassy media such as boric acid. The mean lifetimes observed are rarely greater than a few seconds. The schools of Lewis in the United States and Terenin in the Soviet Union have made notable contributions in this field, which has been reviewed by KASHA [2]. For organic molecules in solution the metastable state is identified as the triplet in which the forbidden nature of the transition involving a change in multiplicity results in lifetimes much longer than those observed in fluorescence. The decay is found to follow an exponential law with respect to time and to be independent of temperature. Phosphorescence from solid crystalline phosphors does not always decay according to an exponential law and is temperature-dependent. The theories proposed to account for it seem at the present stage of development to be distinct from those favoured for organic molecules in solution.

There have been several reports in the literature of interference from phosphorescence with the liquid scintillation counting of tritium [3, 4] although there does not appear to have been any systematic survey or analysis of this phenomenon. This phosphorescence arises from excitation of both the liquid scintillator sample and its container by light irradiation during preparation prior to insertion in the counting equipment. It can produce a significant increase in background, which decays too slowly to be conveniently avoided by waiting but sufficiently rapidly to make correction a nuisance. Under some circumstances the increase in background may be so great that the system is no longer usable [3]. The problem is of greatest significance in single-channel counting systems since phosphorescence is a single photon emission and would not be expected to give rise to coincident pulses in a two-channel apparatus; see, however, HERBERG [3]. Measures which have been taken to minimize the effects of phosphorescence are the use of quartz sample containers and operation at considerably reduced temperatures.

The objectives of the work described in this paper are to establish the relative magnitudes of phosphorescent emission from systems likely to be encountered in tritium assay and to see what steps can be taken to overcome the undesirable effects which may result.

### Experimental methods

The basic experimental procedure consisted of excitation of a sample under standard conditions of illumination, followed by examination of the phosphorescence with a single-channel counter. The counting apparatus used for most of this work was the Ekco N 664 liquid scintillation counter in which the sample bottle rests directly on the photomultiplier face and optical coupling is made with a thin layer of silicone oil. The counter was modified so that the 2 in diameter photomultiplier (E.M.I. type 9514 S) could be temperature-stabilized by a flow of mains

water directly around the tube envelope. No difficulty was experienced from the slight phosphorescence of the mains water or from electrical leakage through the envelope. A diagram of this arrangement is shown in Fig. 1.

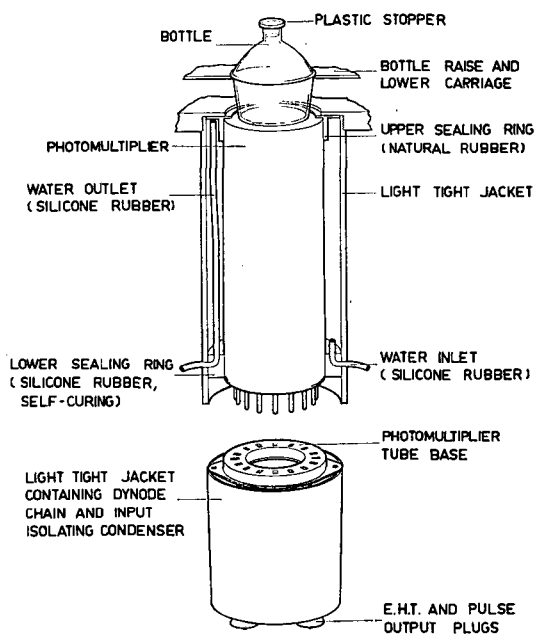


Fig. 1

Photomultiplier and counting bottle assembly.

The pulses from the photomultiplier were fed via a cathode follower with a 5  $\mu\text{sec}$  differentiating time constant to an amplifier (United Kingdom Atomic Energy Research Establishment, Harwell type (1430 A)) with a gain of X 1000. The shaped and amplified pulses were fed to an automatic scaler (Isotope Developments Ltd. type 1700). The output of the divide-by-ten dekatrons of this scaler were used to drive a two-decade logarithmic ratemeter, which finally fed a potentiometric strip-chart recorder. The system therefore allowed determination of the count rate by the scaler and also continuous plotting of the count rate on a logarithmic scale, which accurate switching of ratemeter ranges. The logarithmic display was found particularly suitable under circumstances in which a considerable change in count rate occurred in a short time coupled with a need to determine the approach to, or small changes of, background level.

The basic photon detection efficiency is most easily expressed empirically in terms of tritium counting efficiency; this of course varies with type of sample container and scintillator. A value of 52% efficiency with a background of 39 counts/s was obtained with the following conditions: clear heat-resisting glass bottle ("Pyrex", as supplied by the manufacturers with N 664) containing 4 ml of a 3 g/l solution of p-terphenyl in toluene, spiked with tritiated hexadecane. Comparison of efficiencies under other sample-container and scintillator conditions is given in Table I and will be referred to in detail later. The conditions of ex-

TABLE I  
RELATIVE TRITIUM DETECTION EFFICIENCIES

Scintillator	Scintillator solvent	Dissolved gases present	Type of counting bottle	Type of filter	Detection efficiency*
p-terphenyl	Purified A.R. toluene	Air	Clear "Pyrex"	—	100
p-terphenyl	Purified A.R. toluene	Air	Clear "Pyrex"	"Pyrex" disc	85
p-terphenyl	Purified A.R. toluene	Air	Clear "Pyrex"	Chance	87
p-terphenyl + POPOP	Purified A.R. toluene	Air	Clear "Pyrex"	OX 7 disc	98
p-terphenyl + POPOP	Purified A.R. toluene	Air	Clear "Pyrex"	—	94
p-terphenyl + POPOP	Purified A.R. toluene	Air	Clear "Pyrex"	"Pyrex" disc	94
p-terphenyl + POPOP	Purified A.R. toluene	Air	Clear "Pyrex"	Chance	7
p-terphenyl + POPOP	Purified A.R. toluene	Air	Coated "Pyrex"	OX 7 disc	95
p-terphenyl + POPOP	Purified A.R. toluene	Nitrogen	Coated "Pyrex"	—	133
p-terphenyl	Scintillator grade 'Kinard' mixture	Air	Clear "Pyrex"	"Pyrex disc"	61
p-terphenyl	Purified 'Kinard' mixture	Nitrogen	Clear "Pyrex"	"Pyrex disc"	73

\* Relative to the figure for p-terphenyl (3 g/l) in purified A. R. toluene.

citation were chosen to simulate strong noonday sunlight, this being the most severe condition that would be encountered in practice. This was conveniently reproduced in the laboratory by a Philips 300 W home sun lamp (type 57265/28),

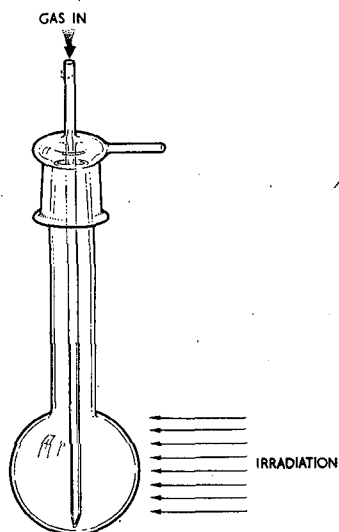


Fig. 2  
Irradiation vessel.

the radiation being filtered through 1 cm of 5% aqueous copper-sulphate solution for adjustment of the spectral composition and the heating effect. Solids were



placed about 15 cm from the face of the lamp, but in view of their varying shapes the irradiation was only approximately constant. For liquids an irradiation container of heat-resisting ("Pyrex") glass, as illustrated in Fig. 2, was used. Arrangements were made for the accurate repositioning of this in the light beam. The container had facilities for the bubbling of gas through the liquid and allowed convenient transfer, via the side arm, of the irradiated liquid into a dark-adapted counting bottle. No absolute measurements of total dose rate or intensity versus wavelength relationships for the lamp were undertaken; however, empirical checks on constancy of performance were made with a uranyl oxalate actinometer [5]. With 4 ml of uranyl oxalate in the standard irradiation container the following rates of decomposition of oxalate were found: Philips lamp, 5.5 mg/min; sunlight

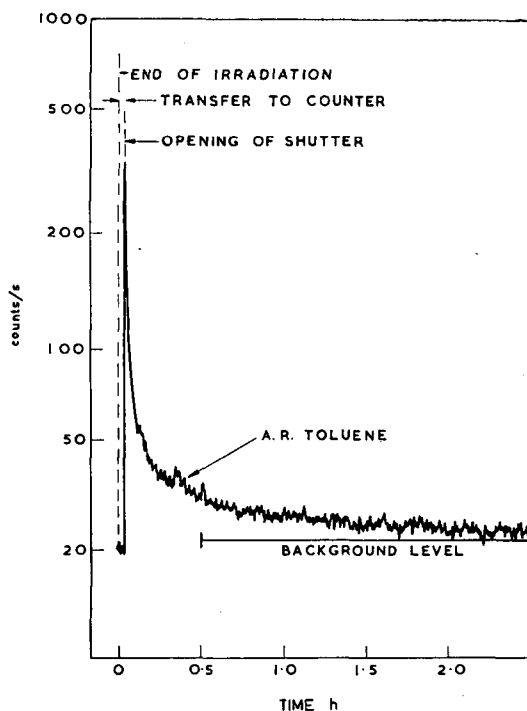


Fig. 3

Recorder trace of phosphorescence versus time. Analytical reagent grade toluene, saturated with nitrogen.

at Wantage, 4.35 mg/min; fluorescent laboratory lighting, nil. For examination of the phosphorescence of liquids it was necessary to irradiate them and then transfer them in the dark, immediately after excitation, to a dark-adapted counting bottle. Four ml of the liquid to be examined was bubbled either with oxygen or oxygen-free nitrogen in the vessel shown in Fig. 2 and then given a timed irradiation under the lamp. Solids were treated according to their physical shape and hence did not always receive identical treatment. Solids other than counting bottles were irradiated in a beaker and then transferred to a wide-mouth counting bottle for counting.

## Results

### PHOSPHORESCENCE IN LIQUIDS — AVOIDANCE BY OPTICAL FILTRATION

Initial investigations suggested that phosphorescence intensity reached saturation level in 2 min irradiation. Although subsequent work on a number of compounds has shown this is not always so, the results refer to an irradiation time of 2 min. The apparatus recorded directly a plot of the logarithm of the count rate versus time, which would yield a straight line in the case of exponential decay of phosphorescence. In no case was this observed. Fig. 3 is a typical trace, obtained with analytical reagent-grade toluene. In many cases it has been found that a plot of the count rate against time is hyperbolic. This is illustrated by the top curve of Fig. 5 which represents the data from Fig. 3 replotted on an inverse time ( $1/T$ ) scale. Most of the data is therefore presented in this form.

The phosphorescence decay curves for a number of solvents and a liquid scintillator are given in Fig. 4. The materials used in these determinations were

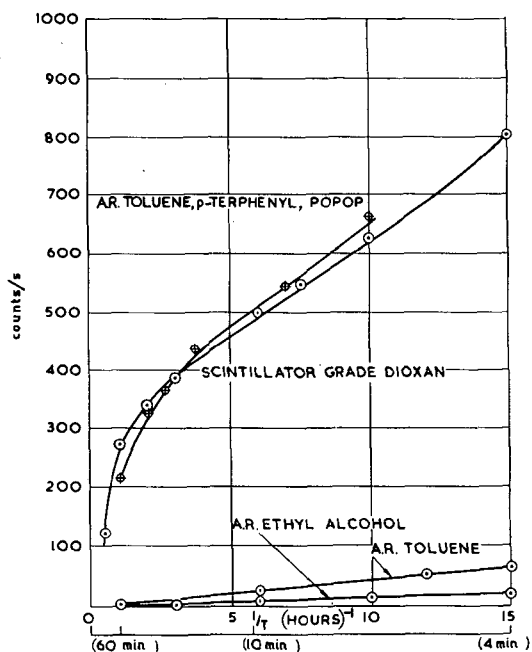


Fig. 4

Phosphorescence versus reciprocal of time for a number of liquid scintillator components, all nitrogen-saturated liquids.

bubbled with oxygen-free nitrogen and kept under an atmosphere of the latter. Subsequent results show that the behaviour of most of these substances is critically dependent on their purity. The compounds however were all either "scintillation grade" chemicals or analytical reagents, i. e. of a purity standard generally used for liquid scintillation counting. The effect of purification of toluene is illustrated in Fig. 6 for measurements made in the presence of nitrogen. The top curve is for "Analar"-grade material and the second for this same material dried over sodium and redistilled before use. The third sample was a high-purity National Chemical

Laboratory standard in which no significant phosphorescence could be observed.

Fig. 6 shows that, as a result of saturation of toluene with oxygen, the phos-

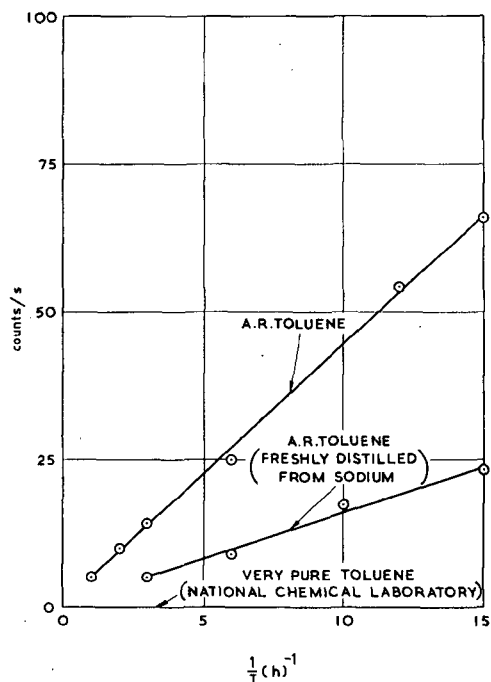


Fig. 5

The effect of solvent purification. Phosphorescence versus reciprocal of time for toluene, nitrogen-saturated.

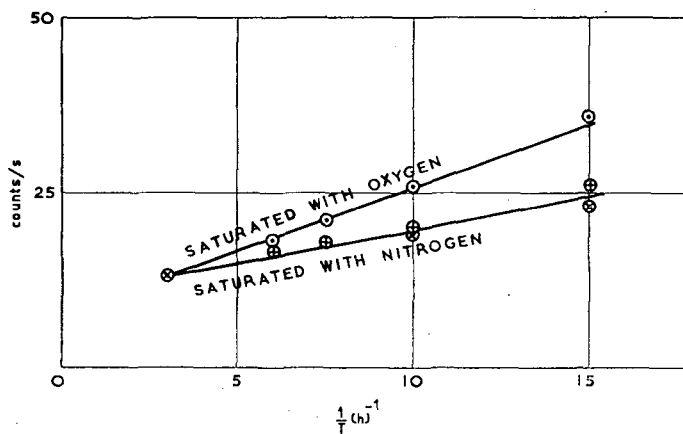


Fig. 6

The effect of oxygen on phosphorescence. Phosphorescence versus reciprocal of time for toluene.

× Original experiment in presence of nitrogen.

+ Experiment on sample which had been previously irradiated in presence of oxygen.

phorescence is increased. Irradiation in the presence of oxygen does not appear to produce a permanent change since the same sample subsequently re-irradiated in the presence of nitrogen shows a phosphorescence decay curve not significantly different from the original values obtained in the absence of oxygen.

Alternative methods to rigorous purification for removal or reduction of phosphorescence were sought. The existing work on very short-lived phosphorescence of the type studied by KASHA [2] has shown that the minimum wavelength of phosphorescence is always greater than the fluorescent wavelength. Experiments were made with spectral filters. The requirement was that a filter should be opaque to the phosphorescent wavelengths but should transmit as efficiently as possible the fluorescent wavelengths on which the counting of the tritium beta particles depends. A glass filter transmitting in the 2500–4000 Å range, Chance 0X7, has been found to be extremely well suited to this purpose. It was inserted in the present apparatus as a 2 mm-thick sheet between the cell and the photomultiplier. Its effectiveness in absorption of phosphorescent radiation is demonstrated in Figs. 7 and 8 for a "Kinard"-type solvent (toluene; dioxan; ethyl alcohol; 5:5:5:3). P-

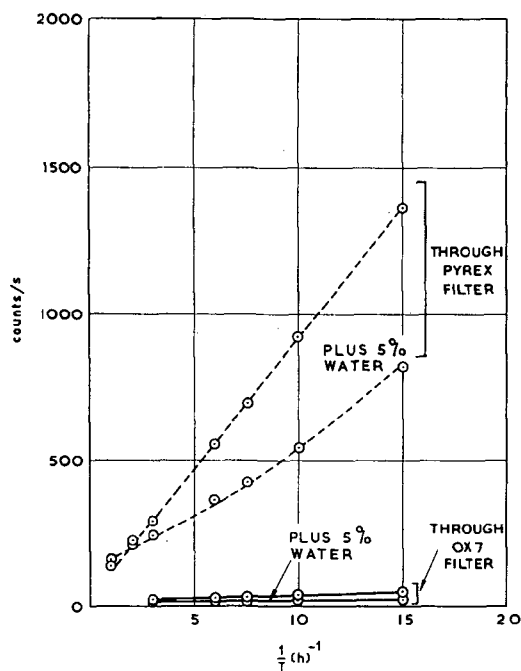


Fig. 7

The effect of spectral filtration on observed phosphorescence. (Chance 0X7 filter). "Kinard" solution prepared from scintillation grade materials saturated with air.

terphenyl was added as the scintillator solute. Two levels of purity were investigated, normal "scintillation grade" or reagent grade and, secondly, solvents which had been freshly purified before use, e.g. with dioxan distilled from sodium, two or three times. Furthermore, since the solvents in the first category were saturated with air while those in the second were nitrogen-bubbled, the two series could be considered to represent reasonably normal limits in care of sample preparation.

The presence of up to 5% water was also investigated. From a brief summary of the data given in these figures it can be seen that in all cases there is a great reduction in the count rate due to phosphorescence when the  $0 \times 7$  filter is in position. The scintillator solution in the higher state of purity shows much less phosphorescence than does the normal grade although the presence of water reduced

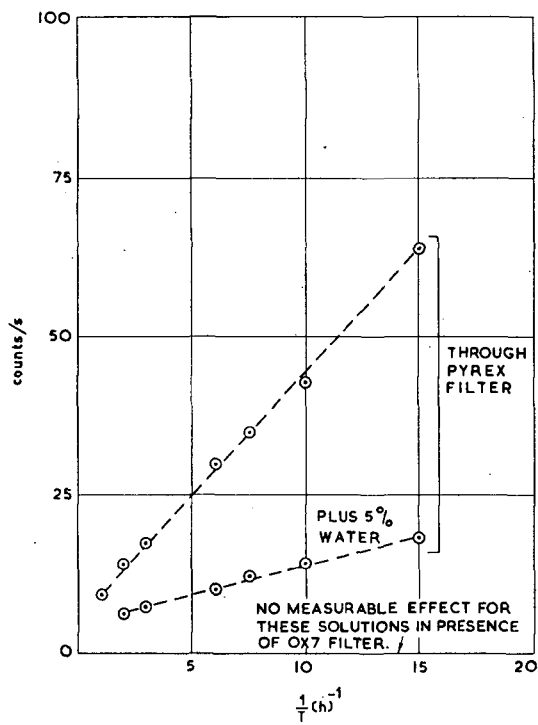


Fig. 8

The effect of spectral filtration on observed phosphorescence (Chance  $0Q7$  filter). "Kinard" solution prepared from freshly purified reagents saturated with nitrogen.

the effect in both cases. The usefulness of such a filter as a practical measure in counting is determined by the amount of fluorescent radiation absorbed and hence the reduction in counting efficiency imposed. This factor is controlled by the scintillator used, which should clearly have an emission spectrum within the transmission limits of the filter. Published data [6] suggest that p-terphenyl should satisfy this condition, and this has been confirmed by efficiency measurements as follows.

#### EFFICIENCY MEASUREMENTS

The tritium-counting efficiency was determined under various conditions, both with and without the  $0 \times 7$  filter. The interposition of the  $0 \times 7$  filter alters the efficiency in two ways: geometrically it raises the counting bottle from the photocathode face, and optically it filters the fluorescent radiation coming from the bottle. For a fair comparison the geometry effect ought to be taken into account, and this was done by comparison of the  $0 \times 7$  filter value with that obtained with a heat-resisting glass ("Pyrex") plate of exactly similar dimensions (referred to as

"Pyrex" filter). The tritium activity was standard hexadecane, supplied by the Radiochemical Centre, Amersham, and dissolved in 4 ml of scintillator, this being the same volume as that used for the phosphorescence measurements. The results are shown in Table I and are expressed relative to p-terphenyl in toluene without any filter. The absolute efficiency under these conditions was 52% with a background of 39 counts/s, the photomultiplier noise contribution being 31 counts/s.

The addition of phenyloxazolephenyloxazolephenyl to move the fluorescent emission to longer wavelengths has generally been regarded as desirable for achievement of matching to the photomultiplier cathode and hence maximum efficiency. (Measurements with this system were therefore included.) As can be seen from the results, no gain in efficiency was found with our apparatus. This result was further investigated by determination of the spectral sensitivity of the actual photomultiplier used. These results, together with curves for the emission spectra of the two scintillators, are given in Fig. 9. No difference in efficiency between the two systems could be

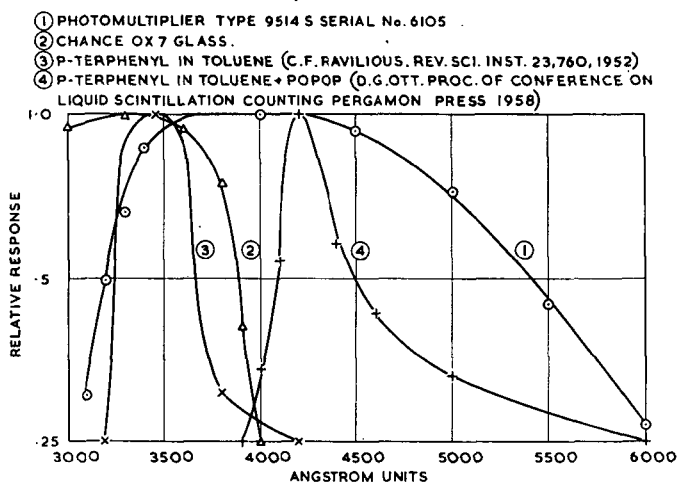


Fig. 9

Spectral response for photomultiplier, relative transmission of Chance filter and fluorescent emission of scintillators.

expected on the basis of spectral matching. It should, however, be borne in mind that comparison of efficiency figures is likely to be specific to an apparatus because of such factors as spectral response of reflectors and self-absorption of fluorescence [7]. When the  $O \times 7$  filter is inserted in the apparatus, a big difference in efficiency is found between these two scintillator systems, the p-terphenyl showing much smaller absorption loss; this would be expected from the spectral curves shown in Fig. 9. It can therefore be concluded that phosphorescence from toluene-dioxan systems can be greatly reduced without significant loss in counting efficiency by the use of the combination of  $O \times 7$  filter and p-terphenyl as scintillator.

#### THE PHOSPHORESCENCE BIAS CURVE

It is known that the count-rate from phosphorescence can be reduced in the same way as that of the photomultiplier noise count, that is, by an increase of the discriminator bias. The increase in bias reduces the counting efficiency, so it is desirable

to know the relationship involved. Measurements were made on a "Pyrex" glass counting bottle which was irradiated for a known time. First the decay curve was measured; and then, after another irradiation for the same time, the bias curve was measured. The bias curve was then corrected for the observed decay, the result thus being the true phosphorescence bias curve. This was compared with the photomultiplier noise bias curve, as shown in Fig. 10, by multiplication of the noise counts

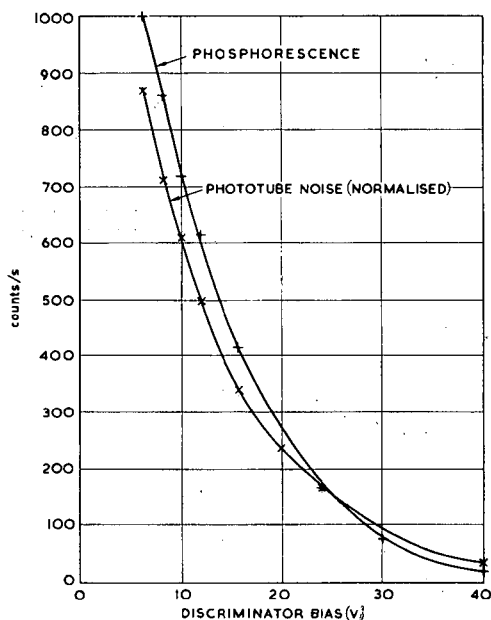


Fig. 10

Phosphorescence versus discriminator bias. Values determined for "Pyrex" (heat-resisting) glass.

by 20 and by plotting on the same scale. It can be seen that there is a close similarity between the shape of the curves, as would be expected if phosphorescence were a process involving single photon emission, as evidenced from measurements with counters using photomultiplier tubes in coincidence. The single photons give rise to single photoelectrons from the cathode, as is also the case in thermionic emission.

It might, therefore, be expected that the energy distributions would be similar. This does seem to be the case although it is known that photomultiplier noise is not entirely due to thermionic emission from the photocathode [8]. Similar considerations lead to the conclusion that the phosphorescence bias curve does not appreciably change as the phosphorescence decays although the phosphorescence spectrum may well change as the decay proceeds. Therefore, although the phosphorescent count can be biased off in the same way as can be the noise count, the efficiency will be affected in a similar manner; and for a particular scintillation counter, the noise/efficiency characteristics can be used for estimation of the sensitivity to phosphorescence.

#### PHOSPHORESCENCE IN SOLIDS — A NON-PHOSPHORESCENT SAMPLE BOTTLE

One of the main sources of phosphorescence in the counting assembly is the counting bottle itself. Ordinary glass is known to be highly phosphorescent and

is sometimes substituted by quartz [9]. A number of solids which could be used to manufacture counting bottles were examined. Difficulty was experienced in irradiation and counting under standard conditions because of the variable shapes of the test samples. The results shown for glass refer to two different types of counting bottles, designated "Pyrex" bottle (1) and "Pyrex" bottle (2), and the results can only be compared quantitatively for each individual type of bottle.

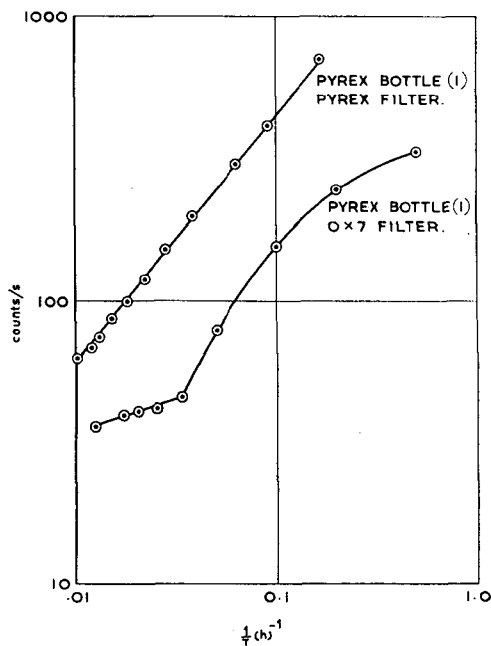


Fig. 11

Phosphorescence of "Pyrex" (heat-resisting) glass. Log count rate versus log reciprocal time.

Fig. 11 shows a typical result from "Pyrex" bottle (1). A straight line is obtained when log counts/s is plotted against log  $(I/T)$  indicating an equation of the form  $I = \left(\frac{1}{T}\right)^a$ , where  $I$  is the phosphorescent intensity. This is a decay law for a photo-conducting phosphor [1]. The  $0 \times 7$  filter reduces the phosphorescence, and the curve then becomes complex. Fig. 12 shows the results from "Pyrex" bottle (2). The curve for the clear bottle with the "Pyrex" filter is approximately linear, the linearity increasing with time. Unfortunately the measurements could not be extended to overlap the time scale for bottle (1) because of the low count rate, but it may be that the straight line for bottle (1) is the tail-end of a more complex curve. Again, the  $0 \times 7$  filter with bottle (2) reduces the phosphorescence and increases the complexity of the curve. There is a suggestion, however, that, even with the  $0 \times 7$  filter, the tails of the curves are linear.

The effect of coating the bottle with a non-transparent reflecting coating is also shown in Fig. 12. As to be expected, by shielding of the glass from exciting light one coat (white) reduces phosphorescence considerably and two coats (undercoat white and top coat black) reduce it even further. It is not essential that the coats themselves be non-phosphorescent provided they are completely opaque. A suitable



coating both reduces bottle phosphorescence and increases counting efficiency. We have found "Rampart" glass writing ink to be a suitable coat\*.

Various other materials have been examined, data on one of which, quartz, are shown in Fig. 12. The quartz, in the form of a disc, was irradiated for 1 min and placed in optical contact with the photomultiplier face. There was a little phosphorescence from this material, and the graph is linear. The counting efficiency

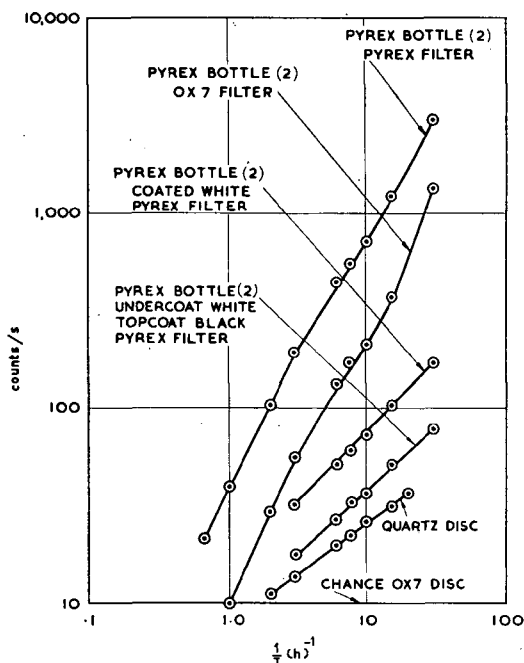


Fig. 12

Phosphorescence of "Pyrex" (heat-resisting) glass and quartz, the effect of spectral filtration (OX7 filter) and coating to reduce absorption of exciting radiation. Log count rate versus log reciprocal time.

in this position is comparable with that of the bottle window. Various transparent plastics exhibited phosphorescence, including methyl methacrylate polymer ("Perspex"), which, although slightly soluble in toluene, would still be suitable as a short-term counting bottle because "Perspex" does not quench the scintillation process.

It was somewhat surprising that, of all the solid materials examined, the only one which was non-phosphorescent was Chance OX7 glass. The use of such a material for a counting bottle would combine the advantages of optical filtration and non-phosphorescence.

#### CHEMILUMINESCENT REACTIONS

It is possible that the luminescence arises from the decay of an electronically-excited species formed as a product of a chemical reaction. Such a process could be dependent on an initial irradiation to produce a reactive species, for example, a

\* Available from A. Gallenkamp and Co. Ltd., London.

radical of long life. Chemiluminescent oxidations of organic compounds have been reported [10]; and, in fact, their kinetics have been followed with a photon counter [11]. Some preliminary experiments to see to what extent such reactions resemble the phosphorescence observed in our experiments have been made. About 0.1 ml of 100 volume hydrogen peroxide was added to 4 ml of dark-adapted dioxan and the light output followed in the standard way. Fig. 13 shows the results. The inten-

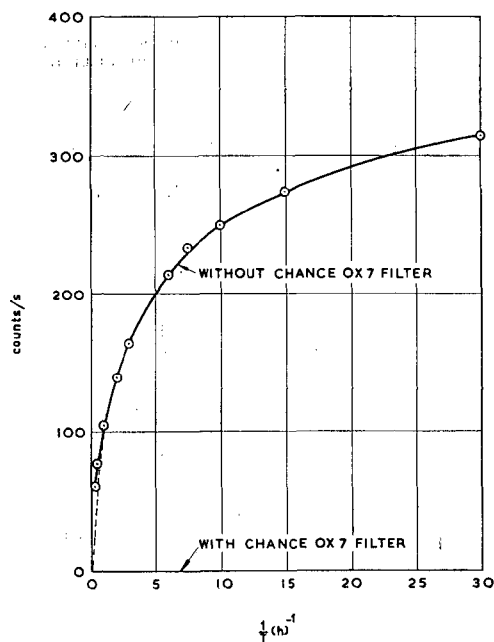


Fig. 13

A chemiluminescent reaction, 4 ml dioxan, 0.1 ml 100 volume hydrogen peroxide, showing the effect of spectral filtration.

sity and decay observed are similar to those for the light-excited phosphorescence of dioxan. Hydrogen peroxide decomposing catalytically on platinum does not give any detectable luminescence; therefore, dioxan or one of its derivatives must be the luminescent material.

The simplest theory is perhaps that hydrogen peroxide is decomposed with the formation of atomic oxygen and that the energy liberated on the formation of molecular oxygen excites the dioxan molecules. This can be compared with the case in which the presence of oxygen in pure solvents gives rise to phosphorescence. It can be argued that the atomic oxygen is formed by irradiation with ultraviolet light and subsequently recombines to give its energy to the solvent. Such a process would lead to the liberation of 59 kcal/mole corresponding to a wavelength which cannot be shorter than 4800 Å. A more extensive study of luminescence spectra of such systems would seem to be warranted.

## Discussion

The phosphorescence arising in solid materials such as the counting bottle is typical of solid-state luminescence which has been extensively studied [1]. The

electron-trap theory can provide an explanation for the shape of the decay curve. The reason why the Chance  $0 \times 7$  glass is non-phosphorescent, even less so than quartz, is not clear; but it could be that either the radiant energy is not absorbed, or not stored, or it is quenched by some internal mechanism so that the stored energy is dissipated by non-radiative transitions.

The results obtained with liquids are more difficult to interpret in the light of existing theories. The long duration of the phosphorescence, of the order of hours, does not fit in with existing theories on triplet-state excitation [2], where lifetimes ranging from milliseconds to seconds have been observed. In addition, the triplet state decay is exponential, while this phosphorescence is better fitted by a hyperbolic decay. It may be that tritium counters are so sensitive that the tail end of a triplet excitation process is being observed and that the hyperbolic decay is arising from some multiple deactivation process such as that suggested by JACKSON *et al* [12]. However, for very pure solvents, long-term phosphorescence is not observed, nor is the existence of the triplet state in this type of compound observed by electron-spin resonance [13].

The long-term decay could possibly be explained on the basis of a chemiluminescent reaction, such as that occurring during the oxidation of an organic compound by hydrogen peroxide [10, 11]. Such a process could explain the non-phosphorescence of pure solvents and their phosphorescence in the presence of oxygen. However, so many chemical reactions could be postulated that it does not seem possible to assign one particular mechanism at the moment merely on the basis of measured kinetics.

A further possibility which has been considered is that the phosphorescence is due to electronic excitation followed by storage of the energy in electron traps, as in the theory of the solid state. It is difficult to see how such a trap may survive, even if it were admitted that a degree of crystalline structure is present over limited regions in the liquid state and that essentially solid-state conditions exist [14]. However, some of the experimental facts can be adequately fitted by the solid-state theory.

Phosphorescence in liquids may be due to more than one of the foregoing processes, depending on the system studied; and further work remains to be done before definitive conclusions can be drawn.

#### ACKNOWLEDGEMENTS

The authors wish to thank all those who have assisted with this work, particularly Professor G. F. J. Garlick for a valuable discussion during its initial phases, and also their many colleagues at the National Chemical Laboratory, Teddington, the Department of Scientific and Industrial Research Unit, Wantage, and the Isotope Research Division, Wantage, Berkshire.

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## DISCUSSION XVII

**D. Sunko** (Yugoslavia): I would like to ask the speaker for a more precise definition of the term "very pure solvent". Was it checked by gas chromatography or any other methods?

**S. Ellis** (United Kingdom): Yes, it was. Obviously, the term "purity" can only be used with respect to some circumstance, some purpose or some specific impurity, but in the case, for instance, of the toluene which we used, the material was of high purity and had been checked by gas chromatography and mass spectrometer. The definition of purity in these cases is that — on analysis — there should be a very high percentage of the compound stated. It is probable that some impurities are present and it is probably fortunate in the case which we chose that these impurities were not phosphorescent. I am quite sure that one could take another compound prepared for a similar purpose and find that, even though it was 99.99% pure, the impurity that it did contain happened to be one which showed phosphorescence or produced a chemiluminescent reaction.

**L. H. Gevantman** (United States of America): In connection with the oxygen effect which he observed, could the speaker tell us whether the same result could occur if the solution were sparged with inert gases?

**S. Ellis**: All I can say is that we have certainly sparged the solutions with nitrogen and have shown (Fig. 6) that the elimination of oxygen reduces phosphorescence. So far as we know, the nitrogen gas in this system is chemically inert, but we have not tried the "inert gases" as such. I can see no reason, however, to expect the results to be substantially different.

**F. Begemann** (Federal Republic of Germany): I wonder whether the hyperbolic decay of your phosphorescence light curve might be caused by the superposition of the decay of many excited levels with various half-lives. Under certain conditions for the population of the various levels at time  $t = 0$ , a hyperbolic decay curve will result rather than an exponential one, as when only one half-life is involved.

**S. Ellis**: I think that this could certainly be so. The view that we are not really concerned with the decay of a triplet state is based on the absence of exponential decay found in other work where the triplet state has been observed, and also on the fact that the period over which we can observe this phosphorescence is very long. But I agree that it could possibly result from the summation of a series of excited states and I would not like to rule this explanation out entirely.

**A. Bainbridge** (New Zealand): We have observed a similar hyperbolic decay of background after subjecting our detector (a gas-phase counter) to some "brutal" treatment under the following conditions in metal-walled containers:

- (1) Raising the temperature above 200 °C;
- (2) Subjecting the wall to "Tesla" coil high voltage treatment;
- (3) Friction of inner wall of counter.

In each case the filling was 10 cm argon + 1 cm alcohol.

S. Ellis: These are all processes which are likely to cause electron-emission from surfaces. The hyperbolic decay is interesting. It could be the result of a bi-molecular reaction which is started off by the "brutal" treatment of the cathode surface.



# RADIO COLUMN CHROMATOGRAPHIC ASSAY OF $H^3$ -LABELLED SUBSTANCES

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Abstract — Résumé — Аннотация — Resumen

**Radio column chromatographic assay of  $H^3$ -labelled substances.** Combined radio-chromatographic investigations of  $H^3$ -labelled substances are an integral part of the majority of biochemical experiments with  $H^3$ -labelled compounds.  $H^3$ -radio paper chromatography yields, in a scanner with a windowless flow counter, a counting efficiency of 0,5–1,5%, depending largely on the thickness of the paper and the self-absorption of the labelled compound.

The radio gas chromatography of tritiated compounds presents no major problem. Successful use is being made of a combination of a gas chromatograph with a flow ionization chamber and vibrating reed electrometer, a system originated by K. E. Wilzbach and P. Riessz, and improved by H. Dutton, L. Mason and L. Blair. Through the use of "Teflon" and silicone-rubber for the insulating parts of the flow ion chamber, it can be operated at close to 300°C.

Radio column chromatography with tritium holds little promise, when the column effluent is spread out as a shallow layer and slowly passes under a windowless flow counter or a scintillation counter, as was successfully tried with  $C^{14}$ . Liquid scintillation spectrometry is likely to be the chosen method. Essentially, there are two different approaches feasible. These have been compared:

1. The column effluent is passed through a coil of plastic scintillator tubing, which is wound around a "Plexiglas" cylinder and placed in a bath of silicone oil in a light pipe with  $TiO_2$ -reflector.

Similarly, the  $H^3$ -containing effluent can be directed through a test vial, filled — very much as in Steinberg's method — with plastic scintillator beads. These two approaches, that operate highly satisfactorily in the case of  $C^{14}$ , offer low counting efficiencies of less than 1% for  $H^3$  due to the unfavourable surface to volume ratio.

2. The column effluent is combined 1:30 with a mixture of 3:2 toluene/ethanol by the action of a magnet-vibrator before being assayed while passing through a  $K^{40}$ -free glass — coiled between the analyser- and monitor-phototubes. In order to ensure a laminar flow and constantly mixed volume ratio, dose-pumps are used for the supply of buffer on the column and of the 30-fold volume of toluene/ethanol. The counting efficiency for  $H^3$  averages 2.5–4% for coils spreading over the whole diameter of the phototubes.

3. The aqueous column effluent is led through an anthracene-filled glass tube and the  $H^3$  counted with close to 1% efficiency.

**Analyse, par radiochromatographie en colonne, de substances marquées par le tritium.** Dans la majorité des cas, les recherches radiochromatographiques combinées portant sur des substances marquées par  $^3H$  font partie intégrante des expériences biochimiques utilisant des composés tritiés. Avec un ensemble comprenant un compteur à balayage continu sans fenêtre, le comptage du tritium par radiochromatographie sur papier est d'un rendement de 0,5 à 1,5%, qui dépend dans une large mesure de l'épaisseur du papier et de l'autoabsorption dans le composé marqué.

La radiochromatographie en phase gazeuse des composés tritiés ne présente pas davantage de difficultés sérieuses. On utilise avec succès un ensemble de chromatographie en phase gazeuse comportant une chambre d'ionisation à courant et un électromètre à lame vibrante. — conçu par K. E. Wilzbach et P. Riessz et perfectionné par H. Dutton, L. Mason et L. Blair. Grâce à l'emploi de «Teflon» et de caoutchouc de silicones pour les éléments isolants de la chambre d'ionisation, cet ensemble peut fonctionner à des températures voisines de 300°C.

Avec le tritium, la radiochromatographie en colonne donne des résultats médiocres, si le liquide sortant de la colonne se répand en une couche mince et passe lentement sous un compteur à balayage continu sans fenêtre ou un compteur à scintillations, alors que le même procédé a donné d'excellente

résultats avec le carbone-14. Aussi est-il probable que l'on adoptera la spectrométrie à scintillations en phase liquide. Elle comporte essentiellement deux procédés différents, que les auteurs ont comparés:

1. Le liquide sortant de la colonne passe à travers un tube scintillateur en matière plastique, enroulé en spirale autour d'un cylindre en «Plexiglas» et placé dans un bain d'huile de silicone, dans un guide de lumière avec réflecteurs en  $\text{TiO}_2$ .

Ou encore, le liquide tritié sortant de la colonne passe par un flacon rempli d'un scintillateur en matière plastique sous forme de perles, comme dans la méthode de Steinberg. Ces deux variantes, qui donnent des résultats très satisfaisants pour le carbone-14, ont un rendement de comptage inférieur à 1% pour le tritium, par suite du rapport défavorable entre la surface et le volume.

2. Avant d'être analysé, le liquide sortant de la colonne est mélangé, dans la proportion de 1 à 30, avec du toluène/éthanol 3:2 au moyen d'un agitateur magnétique; ensuite, on fait passer ce mélange dans un serpentин en verre exempt de potassium-40, entre le phototube d'analyse et celui de contrôle. Afin d'assurer un écoulement laminaire et un rapport constant de volume entre les substances mélangées, des pompes de dosage sont utilisées pour ajouter une substance-tampon à la colonne et pour maintenir le rapport 1:30 du mélange en volume. Le rendement de comptage de  $^3\text{H}$  est de 2,5 à 4% en moyenne, lorsque la spirale couvre tout le diamètre du phototube.

3. Le liquide aqueux sortant de la colonne passe par un tube en verre rempli d'anthracène, et le tritium est compté à 1% près.

**Радиохроматографическое испытание меченных тритием веществ на колонке.** Комбинированные радиохроматографические исследования меченных тритием веществ являются неотъемлемой частью большинства биохимических экспериментов, проводимых с мечеными тритием соединениями. Выход  $\text{H}^3$ -радиохроматограммы на бумаге в разворачивающем устройстве с поточным счетчиком без окошка с эффективностью отсчета в 0,5—1,5% в значительной степени зависит от толщины бумаги и самопоглощения меченого соединения.

Не представляет также больших проблем газовая радиохроматография. Успешно применяется комбинация газовой хроматограммы с поточной ионизационной камерой и электрометром с вибрирующим язычком-система, разработанная К. Э. ВИЛЬЦБАХОМ и П. РИСС и усовершенствованная Г. ДАТТОНОМ, Л. МАСОНОМ и Л. БЛЕОМ, которая при использовании тефлона (Teflon) и кремнистой резины для инсольационных (insulating) частей поточной ионной камеры может функционировать при температуре близкой к 300 °C.

Радиохроматография на колонке с тритием является малообещающей, когда эфлюент колонки разбрасывается мелким слоем и медленно проходит под поточным счетчиком без окошка или под сцинтилляционным счетчиком, как это успешно было проведено с  $\text{C}^{14}$ . Спектрометрия жидкостной сцинтилляции является удачным методом для выбора.

По существу имеется два различных подхода, сравнение которых приводится ниже:

1. Эфлюент колонки проходит через обмотку трубопровода пластикового сцинтиллятора. Трубопровод наматывается на цилиндр из плексигласа и устанавливается в ванночку с кремнистым маслом в световой трубе с рефлектором  $\text{TiO}_2$ .

Подобным образом эфлюент с содержанием  $\text{H}^3$  можно направить через исследуемую ампулу, наполненную — подобно тому как это делается по методу ШТЕЙНБЕРГА, — пластиковыми шариками сцинтиллятора. Эти два подхода, оказавшиеся вполне удовлетворительными в случае с  $\text{C}^{14}$ , имеют низкую эффективность счета для трития, т.е. менее 1%, из-за неблагоприятной поверхности в отношении объемного соотношения.

2. Эфлюент колонки объединяется при соотношении 1:30 со смесью толуол/этанол в соотношении 3:2 при помощи магнитного вибратора еще до испытания, т.е. во время прохождения через стеклянный сосуд из  $\text{K}^{40}$  между фототрубками анализатора и монитора. Для обеспечения ламинарного потока и постоянно смешанного объемного соотношения применяются дозировочные насосы по созданию на колонке амортизатора и 30-fold объема толуола/этанола. Эффектив-



ность счета трития колеблется в среднем от 2,5 до 4 % для катушек, распространяющихся по всему диаметру фототрубок.

3. Эфлюент водяной колонки пропускается через наполненный антраценом стеклянный сосуд, и подсчет  $H^3$  производится с точностью, близкой 1%.

**Análisis por radiocromatografía en columna de sustancias marcadas con  $^3H$ .** En la mayoría de los casos, las determinaciones radiocromatográficas combinadas de compuestos tritiados forman parte integrante de los experimentos bioquímicos con compuestos marcados con  $^3H$ . Al emplear aparatos de exploración con contadores de flujo sin ventana, la radiocromatografía sobre papel de los compuestos tritiados da rendimientos de recuento del 0,5 al 1,5%, según el espesor del papel y la autoabsorción en el compuesto marcado. La radiocromatografía en fase gaseosa de dichos compuestos tampoco presenta problemas serios. Se emplea con éxito la cromatografía en fase gaseosa, combinada con la aplicación de una cámara de ionización de flujo y un electrómetro de lengüeta vibratoria. Se trata de un sistema ideado por K. E. Wilzbach y P. Riessz, y mejorado por H. Dutton, L. Mason y L. Blair, que puede utilizarse a temperaturas hasta de 300°C si se emplean "Teflon" y siliconas para las partes aislantes de la cámara de ionización.

La radiocromatografía en columna de los compuestos tritiados no ofrece perspectivas favorables si se emplea el método, tan eficaz en el caso del  $^{14}C$ , que consiste en extender el efluente en una capa de poco espesor que se hace pasar lentamente por debajo de un contador de flujo sin ventana o de un contador de centelleo. Probablemente se terminará por adoptar como método de trabajo la espectrometría de centelleo del líquido. Fundamentalmente existen dos maneras de operar, que el autor ha comparado:

1. El efluente de la columna se hace circular por un tubo de material plástico centelleador arrollado en espiral alrededor de un cilindro de "Plexiglas" que se coloca en un baño de aceite de silicona contenido en una guía óptica con reflector de  $TiO_2$ .

También se puede hacer pasar el efluente conteniendo tritio por un frasco relleno con cuentas de un centelleador de material plástico, como en el método de Steinberg. Las dos variantes dan excelentes resultados en el caso del  $^{14}C$ , pero en el del  $^3H$  el rendimiento de recuento es inferior al 1% debido a que la razón superficie/volumen es desfavorable.

2. Por medio de un agitador magnético se mezcla el efluente de la columna en la proporción 1:30 con tolueno/etanol 3:2; seguidamente se analiza esta mezcla haciéndola circular por un serpentín de vidrio, exento de  $^{40}K$ , situada entre el fototubo analizador y el de control. La solución tampón se añade por medio de bombas dosificadoras, igual que el volumen necesario de la mezcla tolueno/etanol, y con ello se aseguran un flujo laminar y una proporción constante en la mezcla final. El rendimiento de recuento del  $^3H$  cuando el serpentín abarca todo el diámetro de los fototubos oscila en general entre 2,5 y 4%.

3. El efluente acuoso de la columna se hace pasar por un tubo de vidrio relleno de antraceno y el recuento del  $^3H$  se efectúa con un rendimiento del orden del 1 por ciento.

## Introduction

Combined radio-chromatographic methods have become of great importance in the various branches of tracer work. Despite initial difficulties with weak beta-emitters, such as  $C^{14}$  and  $H^3$ , satisfactory assay techniques for radio paper chromatographic and radio gas chromatographic testing of  $C^{14}$ - and  $H^3$ -labelled compounds, which make use of the whole spectrum of suitable radiation detectors have been developed (see Table I).

For many experimental purposes also, the combination of column chromatographic separation and activity assay of the obtained fractions holds special promise. This applies particularly to the vast field of pathway studies as well as to the exploration of metabolic interactions and of reaction chains. It also commands a certain attention in the field of hot atomic chemistry, such as for the isolation of radiation-labelled compounds.

Used in connection with penetrating radiation, combined radio column chromato-

TABLE I

**PROPOSED RADIO PAPER AND GAS CHROMATOGRAPHIC TESTING METHODS  
FOR COMPOUNDS LABELLED WITH SOFT BETA-EMITTERS.**

Radio paper chromatographic devices for nuclides with soft beta-radiation	Radio gas chromatographic devices for nuclides with soft beta-radiation
Geiger-Müller counter: FULLER [1]	Proportional flow counter: WOLFGANG and ROWLAND [12]
Proportional flow counter: BENSON and CALVIN [2]	Flow ionization chamber: WILZBACH and RIESZ [13]
WINTERINGHAM [3]	MASON, DUTTON and BLAIR [14]
ROBERTS and CARLETON [4]	NYSTROM [15]
Scintillation counter: STEENBERG and BENSON [5]	GANT [16]
Liquid scintillation counter: WILSON [6]	SCHARPENSEEL [17]
SCHARPENSEEL and MENKE [7]	Liquid scintillation counter: PACKARD [18]
Two-dimensional counting devices: GILBERT and KEENE [8]	SCHARPENSEEL and MENKE [7]
ARONOFF [9]	
WINTERINGHAM [10]	
PACKARD [11]	

graphy does not result in any special complications. DOBBS [19] describes a simple way of monitoring the activity of column effluents by means of a Geiger-Müller counter. MENKE [20] separated the various vitamin B-12 analogues of animal tissues and excretions on Dowex 50×4 resin columns and assayed their Co<sup>60</sup>-activity by passing the column effluent through a coil of plastic tube superimposed on the head of a NaJ-scintillation counter. SCHRAM and LOMBAERT [21] used a scintillation counter for the activity measurement of C<sup>14</sup>- and S<sup>35</sup>-column effluents which were evenly spread in a thin layer over the top of a plastic scintillator; for the sake of background suppression this scintillator was arranged in coincidence and yielded a counting rate comparable to that of a G-M end-window counter without self-absorption losses.

After thorough consideration of all pertinent radiation detection devices, the authors consider the liquid scintillation spectrometer unchallengeable for combined column chromatographic and radiation assay of compounds labelled with soft beta-emitters.

The independence of self-absorption losses (homogenous counting) and flexibility with regard to shape and size of the sample opens several intriguing approaches towards direct combination of column chromatography and activity test.

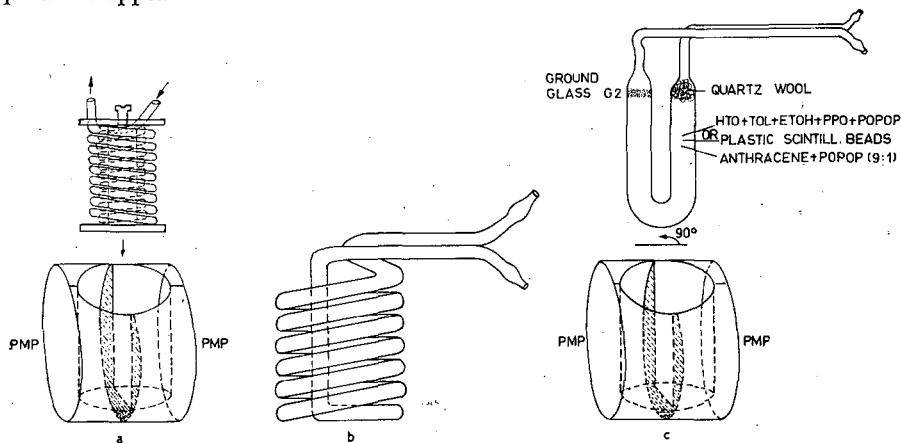
Thus, the authors were running radio column chromatograms of the S<sup>35</sup>-methionin metabolite in chicken [22] and of acid hydrolysis — as well as alkali digestion-products of humic acid and precursors, labelled with C<sup>14</sup> and H<sup>3</sup> [23]. Column effluents with C<sup>14</sup>- or S<sup>35</sup>-labelled fractions can be satisfactorily monitored, with 6–12% counting yield, when passing through a plastic scintillator coil or a bent glass tube with plastic scintillator beads (e. g. Nuclear Enterprises, Ltd., Edinburgh, Scotland: NE 102 plastic scintillator tube of 0.7 mm inner diameter or plastic scintillator beads of 0.5 mm diameter) (Figs. 1a and c). However, short-range H<sup>3</sup>-labelled fractions yield net count rates of less than 0.1% overall counting efficiency (Table II). The surface/volume ratio of the plastic scintillator tube (0.7 mm inner diameter) and beads (0.5 mm diameter) is too low in the case of the extremely weak tritium betas.

TABLE II  
COUNTING EFFICIENCY OF  $H^3$  IN RADIO COLUMN CHROMATOGRAPHY  
UNDER DIFFERENT EXPERIMENTAL APPROACHES

		HTO in Plastic Scintillator		HTO+Toluene+ +Ethanol (1:9:6)+ +PPO+POPOP in a bent glass tube of 4 ml volume		HTO+Toluene+ +Ethanol (1:9:6)+ +PPP+POPOP in a glass coil of 10 ml volume		HTO in a bent glass tube of 4 ml volume with Anthracene+ +POPOP (9:1)	
		beads 0,5 mm dia- meter	tube 0,7 mm inner dia- meter						
Channel V		10-75	10-75	10-75	10-∞	10-75	10-∞	10-75	10-∞
Tp	V	(% counting efficiency)							
5	980			0.025	0.029	0.081	0.081	0.086	0.10
6	1060			0.19	0.21	0.362	0.39	0.23	0.25
7	1140			0.94	0.96	0.957	1.00	0.44	0.47
8	1220	0.036	0.029	3.70	3.74	1.47	1.56	0.55	0.63
9	1300			4.41	5.63	1.82	1.86	0.65	0.79
10	1380			4.43	5.25	1.61	1.92	0.59	0.87
11	1460			3.70	5.68	1.48	2.18	0.52	1.00

### Methods for the assaying of tritium-labelled substances

For activity-assaying of tritium-labelled column effluents two experimental approaches appear most feasible:



THE DIFFERENT COUNTING SYSTEMS: a = PLASTIC SCINTILLATOR COIL IN LIGHT GUIDE  
b = GLASS COIL (JENA GERÄTEGLAS 20)  
c = BENT GLASS TUBE WITH GROUND GLASS FRIT IN LIGHT GUIDE

Fig. 1

The different approaches for radio column chromatography of  $H^3$ -labelled compounds.

1. The aqueous  $H^3$ -effluent passing through a bent glass tube, whose two branches are both facing the two photomultipliers and are filled with a combination of finely ground, water-insoluble primary and secondary organic scintillators. Anthracene + POPOP (9:1) proved to be a useful mixture. Since a certain pressure is required for transportation of the aqueous effluent through the narrow pore space

of the finely ground scintillator powder ( $< 0.1$  mm diameter), one end of the bent glass tube should be terminated by a G 2 ground glass frit (Fig. 1 c). The bent glass tube is accommodated in a cylindrical light guide, which is cut in two halves and coated with a reflector outside as well as in the middle plane and with only the cross section of the centre bore hole left free. This bore hole around the bent glass tube is filled with silicone oil. Thus, this type of light guide assures continuous optical contact with the two photomultiplier windows and increases the counting efficiency of tritium by about 30% (HORROCKS and STUDIER [24, 25], SCHARPENSEEL [26]).

2. The  $H^3$  effluent (aqueous or organic) passing through a bent glass tube or a glass coil (Figs. 1 b and c) is previously mixed with a solution of 60% toluene + PPO + POPOP and 40% methanol. Before it reaches the glass tube or coil between the two photomultipliers, the ternary system is thoroughly mixed by thin steel wires on top of a magnet vibrator. While measuring the activity of the aqueous effluent directly, as, for example, in the anthracene tube, facilitates subsequent peak identification in the effluent fractions stored in a fraction collector, it is difficult to perform further identification work when the aqueous effluent has been mixed with toluene + organic scintillators + ethanol before the activity test.

Fig. 1 shows a plastic scintillator coil, a bent glass tube for Anthracene + POPOP or plastic scintillator beads, and a glass coil from K-free heat resisting glass (Jena Gerätglas 20) which can be used to accommodate the  $H^3$ -labelled column effluent directly or after the effluent has previously been combined with toluene + ethanol + organic scintillators when passing between the two photomultipliers.

### Overall counting yield

In Table II the counting efficiencies of these different methods are compared over the scale of different voltage taps and within discriminator channels of 10–75 V and 10– $\infty$  V. While plastic scintillator beads and a coil of plastic scintillator tubing are both unfeasible with counting efficiencies of less than 0.1%, use of the bent glass tube with finely ground Anthracene + POPOP results in an integral counting efficiency of 1%, whereas the use of the glass coil and of the bent glass tube with aqueous effluent + toluene + ethanol + PPO + POPOP (1 : 18 : 12) provides maximum counting efficiencies of 2% and 5% respectively.

### Instruments

The basic principle of the whole experimental set-up is pictured in Fig. 2. The column effluent moves through a narrow plastic tube of 1.5 mm diam. towards a bent tube with Anthracene + POPOP crystals immersed in the silicone oil of the light guide between the two phototubes of a Tri Carb liquid scintillation spectrometer. It is then channelled into a fraction collector in order to keep the active fractions for further identification work.

In the case of previous mixing of the aqueous column effluent with toluene + ethanol, e.g. in proportions of 1 : 30, the buffer or other eluting agent is pumped in the column by a constant flow-rate dosis pump (Dosis pumps, E. Haage, Mülheim/Ruhr, West Germany). The buffer is stored in a cylindrical vessel with a tight-fitting piston that is floating on the solvents surface for protection against aeration of buffer and column [27].

In fixed proportions (e.g. 30 : 1) toluene + ethanol are combined with the effluent underneath the column by another dosis pump. The resulting ternary system is

completely homogenized when passing a U-shaped knee of glass tubing over the head plate of a magnet stirrer, where thin steel wires vibrate rapidly. In this way an enrichment of the solvent with  $O_2$  during the mixing procedure is avoided. The solvent mixture then flows through black lacquer-coated glass or metal tubes of 3 mm inner diameter to the optical chamber and from here to a fraction collector or a container to be discarded.

Since the Tri Carb liquid scintillation spectrometer does not have a ratemeter

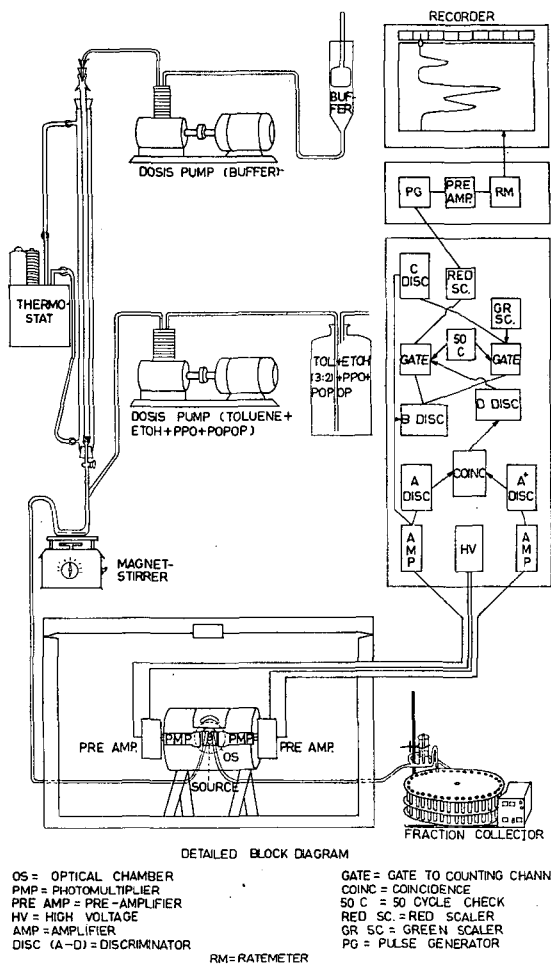


Fig. 2

Principal layout of the instrumental arrangement for column separation and subsequent test of radiation.

and recorder connection, a conventional equipment for radiation detection (FH 49 Frieske and Höpfner, Erlangen-Bruck, Germany) was hooked onto the spectrometer, transferring its activity signals via a ratemeter to a compensograph recorder. (Transistor 2 N 427 red, TP 22, of the last red scaler decade of the spectrometer was

connected to the FH 49 via a condensor, Tüchel-joint and shielded cable. It was synchronized with the latter's scaler by means of a pulse trafo, preamplifier and ratemeter.)

Fig. 3 shows the assembled instruments for combined column chromatographic separation and radiation detection. On the left side is the deep freezer with the optical chamber; extending beyond is the column with two dosis pumps, which transport the buffer from the higher cylindrical storage vessel to the column and

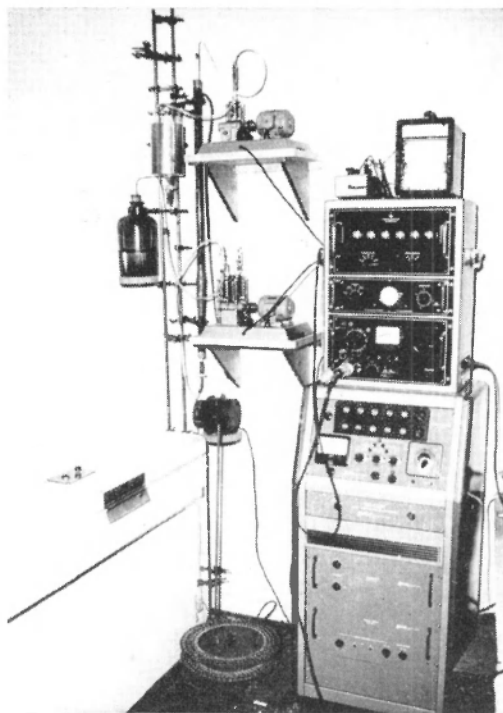


Fig. 3

Assembled equipment for radio column chromatographic assay of  $H^3$ -labelled compounds.

the toluene + ethanol + scintillator solution from the lower brown glass bottle (brown, to preclude disturbances by chemoluminescence) to the junction with the column effluent for subsequent mixing by the magnet vibrator. On the right side are the Tri Carb liquid scintillation counter, standing under the interconnected counting set with ratemeter (FH 49), and the recorder with zero- and full-scale adapter. In between, on the bottom level, stands the fraction collector with continuously adjustable siphon size.

A top view of the glass coil, embedded in an aluminium reflector between the two phototubes and preamplifiers, is pictured in Fig. 4. The glass coil is interconnected with the adjacent glass tubes by "Teflon" transitions. The mixing of the aqueous column effluent with toluene + ethanol + organic scintillator was formerly done by discharge of the column effluent through very fine holes in a plastic tube directly on top of a steel wire 15 mm in length, sticking into the open end of the plastic tube. This steel wire vibrated in front of a magnet stirrer and distributed the aqueous droplets evenly in the toluene-ethanol mixture.

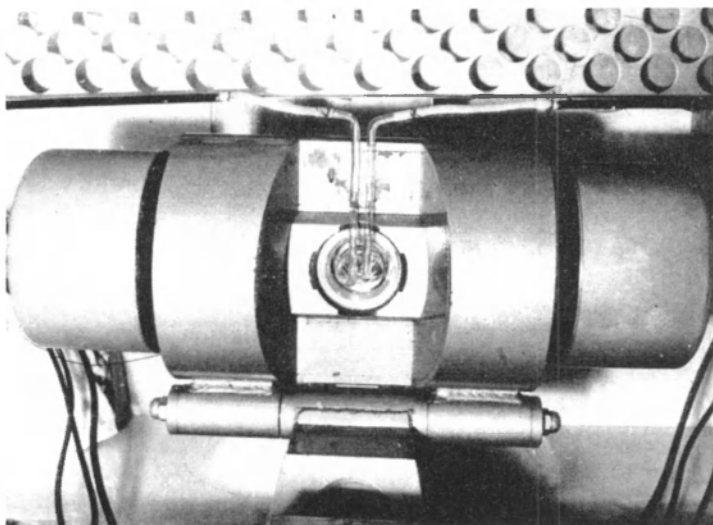


Fig. 4

Top view of the glass coil for flow measurement of the ternary effluent toluene-ethanol-system, embedded in an aluminium reflector between the two photomultipliers.

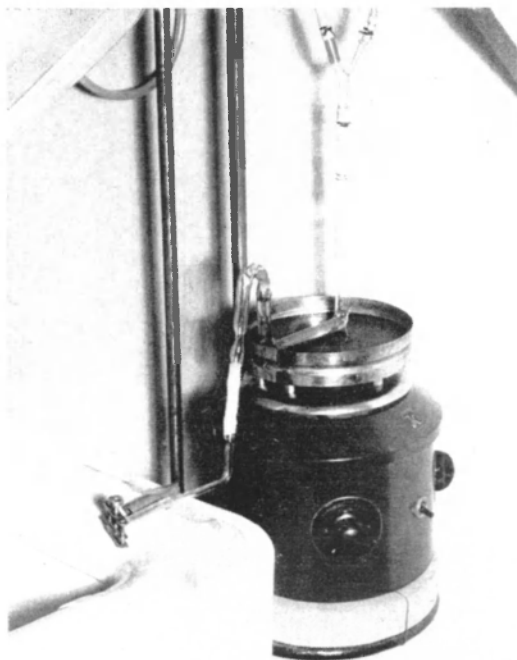


Fig. 5

Mixing of toluene, ethanol and aqueous column effluent in a glass tube by steel rods vibrating on top of a magnet stirrer.

Later it was found that passing of the column effluent + toluene + ethanol through a U-shaped glass tube containing five to six thin steel wires 4 cm in length, with the glass tube standing directly on a magnet stirrer (Fig. 5), gives more perfect homogenization.

#### Factors influencing the counting efficiency

The effect of good mixing by a magnet vibrator is confirmed by Fig. 6. After injection of identical amounts of HTO the mixing mechanism was once put in operation, once switched out. The graph shows clearly that the activity peak is

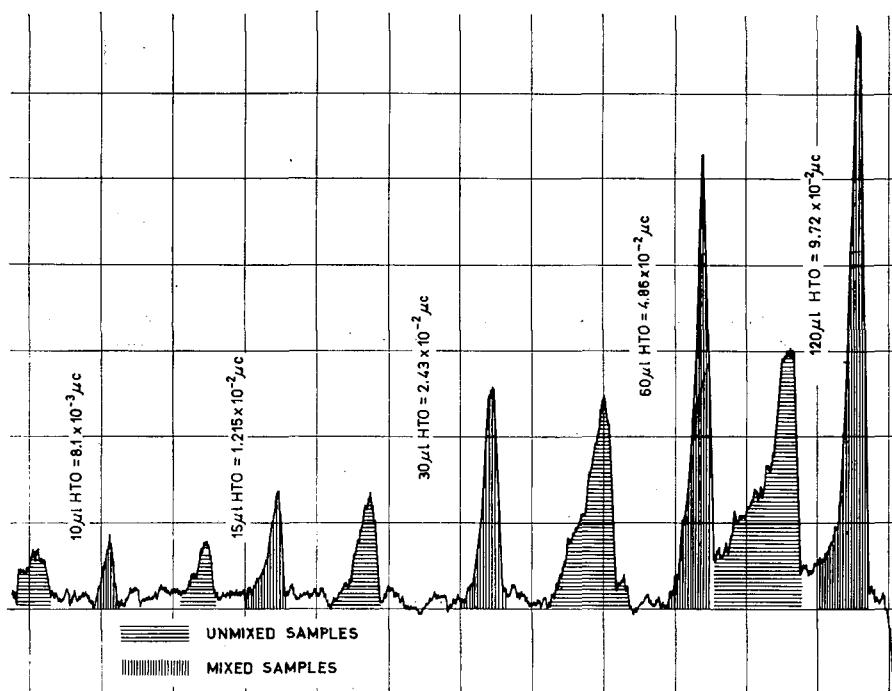


Fig. 6

Effect of mixing the aqueous column effluent and toluene/ethanol-solvent with a magnet vibrator.

smaller and almost twice as high when aqueous effluent and toluene + ethanol + organic scintillators have been mixed by the steel rods over the magnet vibrator. Thus, the mixing step improves the shape of the radio-chromatographic curve as well as the detection sensitivity for small peaks.

In a demonstration of the range of the two different methods and the minimum fraction activities that still produce a sufficient peak size, decreasing amounts of activity were injected into the flow of liquid.

Fig. 7 shows near-proportionality between peak height and fraction activity when the aqueous column effluent passes through a bent tube with anthracene + POPOP (9:1), as referred to in Fig. 1 and Table II. Even a fraction activity of  $4.5 \times 10^{-3} \mu\text{c}$  (approximately 10 000 dpm) produces a prominent peak. Considering that the curves have been recorded on a  $3 \times 10^2$ -scale with attenuation factor of two, fraction activities of about 5000 dpm, even without attenuation, still yield definite peak areas.



When the column effluent is tested for its activity after previous homogenization with toluene + ethanol, the overall efficiency is somewhat higher (Table II). If the column effluent is an organic solvent with only slight quenching properties, the counting yield is the highest obtainable. In Fig. 8 increasing amounts of toluene- $H^3$

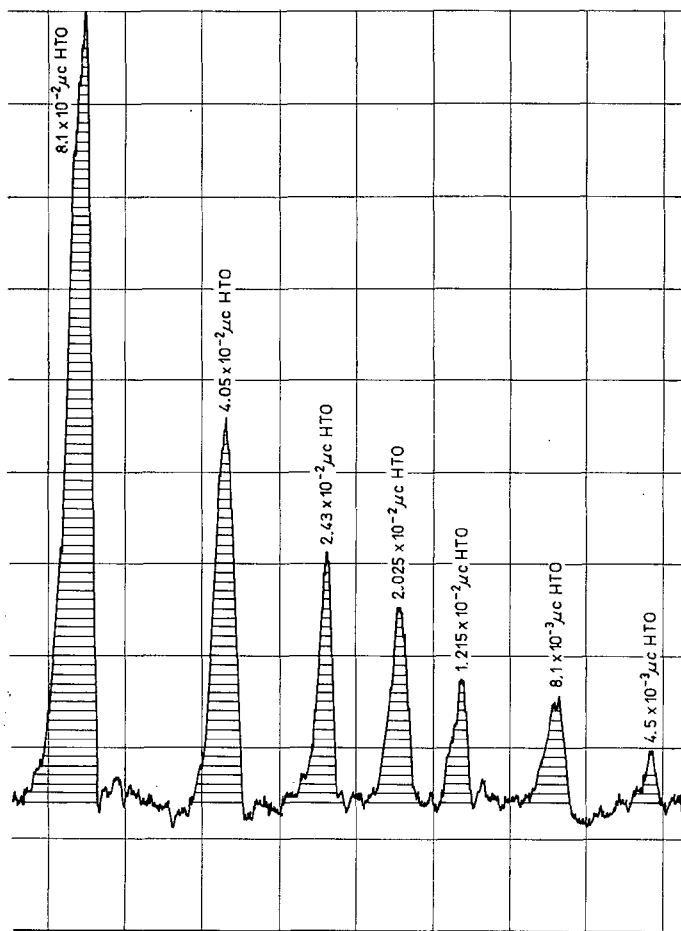


Fig. 7

Flow diagram of counting sensitivity for  $HTO$  passing through a bent glass tube with anthracene + POPOP (90 : 10) — crystals (full distance of paper = 600 counts/min.

were injected into the solvent flow. The relative increase in peak height per injected activity unit shows a slightly regressive trend with increasing amounts of administered toluene- $H^3$ . The lowest activity still producing a representative peak is  $8.6 \times 10^{-4} \mu c$  (approximately 2 000 dpm). In a recorder scale of  $3 \times 10^2$  without an attenuation factor of two, 1 000 dpm would suffice to produce a definite peak area.

In the case of aqueous column effluents, the quenching effect of the 3.3%  $H_2O$  in the ternary system ( $H_2O$  : toluene : ethanol = 1 : 18 : 12) reduces the counting

efficiency. Fig. 9 shows that the smallest activity rate still yielding a well-defined peak is about  $2.5 \times 10^{-3} \mu\text{c H}^3$  (about 6 000 dpm; in a  $3 \times 10^2$  counts/min scale without an attenuation factor of two, about 3 000 dpm). This applies to one part of aqueous column effluent in 30 parts toluene + ethanol (3 : 2).

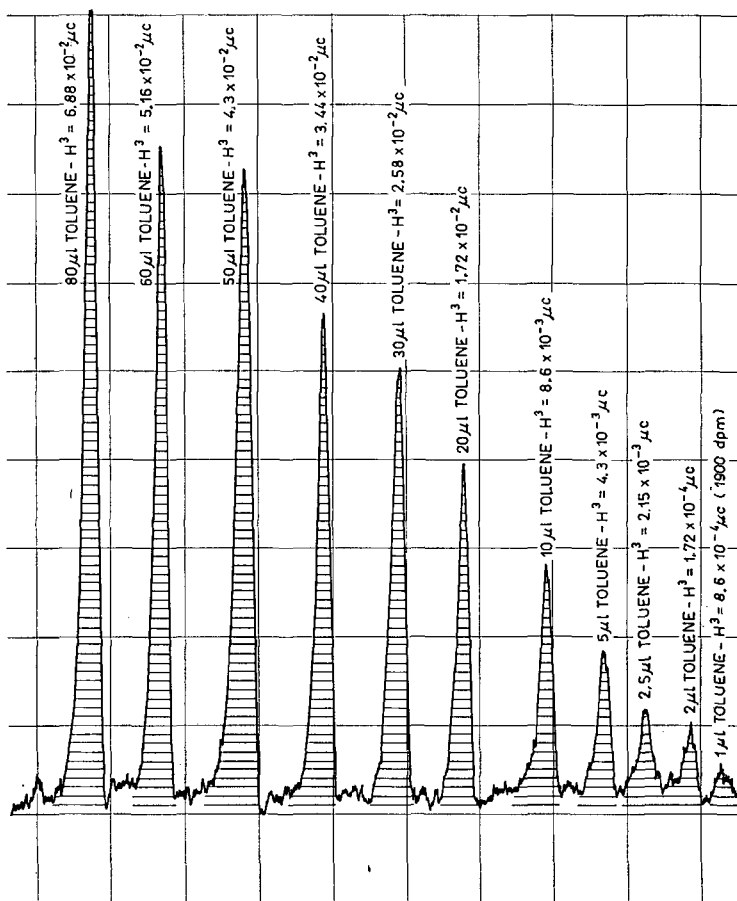


Fig. 8

Sensitivity for toluene - H<sup>3</sup> + toluene + PPO + POPOP (glass coil) (peak height in flow diagram, full distance of paper = 600 counts/min).

If increasing amounts of H<sub>2</sub>O are injected with the same HTO-activity in the flow of solvent, only a slight decrease in counting efficiency is noticeable due to the marked diffusion and dilution of the water in larger volumes of solvent (Fig. 10). When, however, the bent glass tube is filled with HTO-toluene-ethanol mixtures with different proportions of water in the presence of the same amount of H<sup>3</sup>-activity, the conditions illustrated in Fig. 11 are observed. From 0.5—2.5% H<sub>2</sub>O-content the counting efficiency decreases only slightly, from 1.21% to 1.00% (tap 8, 10—75 V window). Then from 2.5 to 7.5% H<sub>2</sub>O a sharp decrease in the counting rate parallels the increasing water content. At 7.5% H<sub>2</sub>O content the

solution is already turbid, indicating uneven distribution of the water in the toluene-ethanol solution. In excess of 10%  $H_2O$  content the water remains partially in the form of droplets. Over-saturation with water and appearance of immiscible water droplets results in a further dramatic decrease of counting efficiency. It is

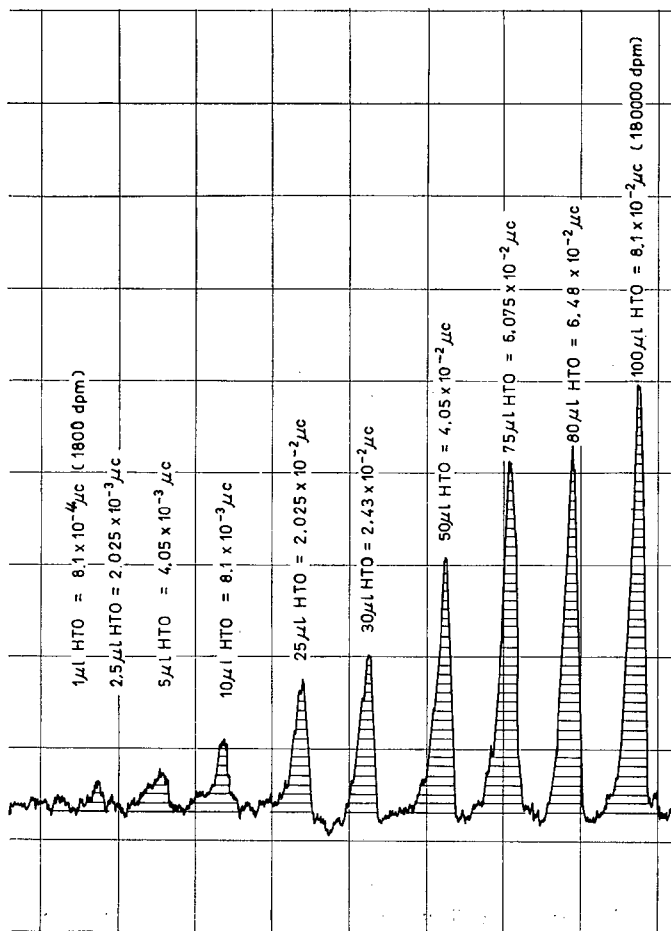


Fig. 9

Sensitivity for HTO in toluene + ethanol (3:2) + PPO + POPOP (glass coil) (peak height in flow diagram, full distance of paper = 600 counts/min).

thus futile to admit more than 5–6%  $H_2O$  in toluene + ethanol since the excessive water droplets coalesce. Their activity evades counting, and the proportionality between true activity and peak area (stable flow speed presumed) is destroyed.

### Examples of radio column chromatographic fractionation

An account is now given of radio column chromatographic fractionation of  $H^3$ -humic acid hydrolysate as well as of the hydrolysis products of randomly

$H^3$ -labelled plant material, which was produced by means of biosynthesis of plant seedlings in HTO-containing nutrient solution.

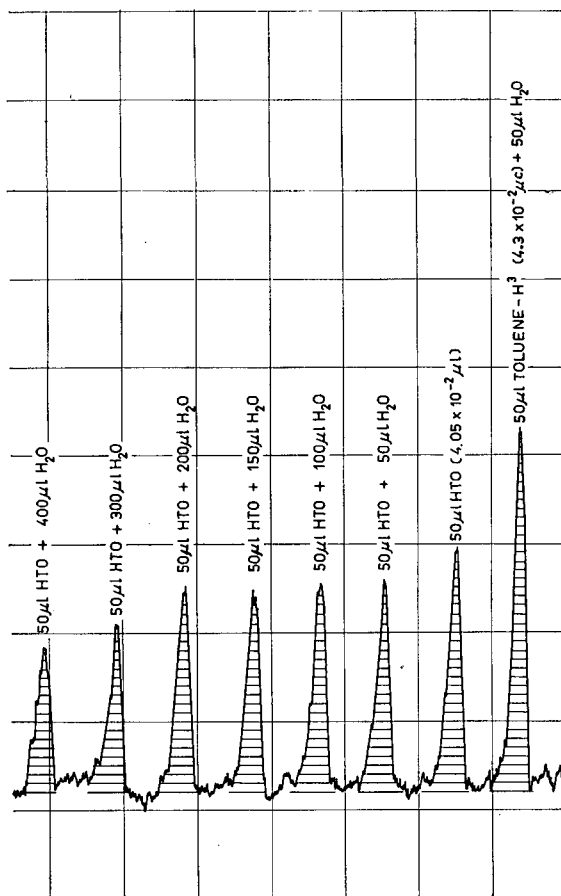


Fig. 10

Direct injection before the mixing vibrator of constant rates of HTO under increasing attenuation with  $H_2O$  (peak height of single injections in flow diagram, full distance of paper = 600 counts/min).

A. RADIO COLUMN CHROMATOGRAPHIC ASSAY OF A 5 N HCl HYDROLYSATE OF  $H^3$ -LABELLED HUMIC ACID BY DIRECT FLOW OF THE AQUEOUS  $H^3$ -EFFLUENT THROUGH A BENT GLASS TUBE WITH ANTHRACENE + POPOP

The fractionation was performed with a 150 cm Amberlite CG 120 column, with particle diameter of  $56 \pm 9 \mu$ , using MOORE and STEIN's [28] citrate buffers of pH 3.25 and pH 4.25 as well as 0.02 N NaOH. The column was heated to  $40^\circ C$  during the first 300 ml and to  $50^\circ C$  for the rest of 400 ml effluent.

Fig. 12 shows the flow diagram of the recorded fraction peaks. The major part of the hydrolyzed fractions appears at the beginning as strongly acidic components (higher organic acids, acidic phenolic compounds) and at the end as stronger basic

components (lysin as well as histidin, tryptophan, arginin, other unidentified indole and stronger basic compounds).

In between are various acidic and neutral amino acid fractions separated and identified in the effluent portions of the fraction collector.

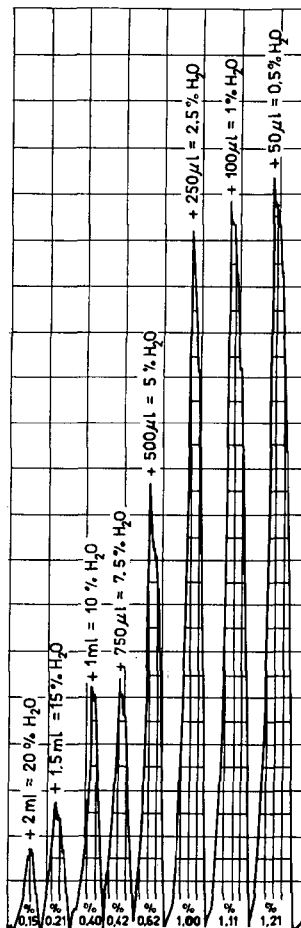


Fig. 11

Counting efficiencies of  $4.3 \times 10^{-2} \mu C H^3$  in a toluene-ethanol (3:2) system under addition of increasing percentage amounts of  $H_2O$  (in a Jena-glass coil of 10 ml volume, full distance of paper = 600 counts/min).

B. RADIO-COLUMN CHROMATOGRAPHIC ASSAY OF A 5 N HCl HYDROLYSATE OF  $H^3$ -LABELLED HUMIC ACID BY MIXING THE EFFLUENT 1:30 WITH TOLUENE + ORGANIC SCINTILLATOR + ETHANOL AND PASSING IT THROUGH A GLASS COIL BETWEEN THE PHOTOTUBES

Fig. 13 shows the flow diagram with peak identification as under A.

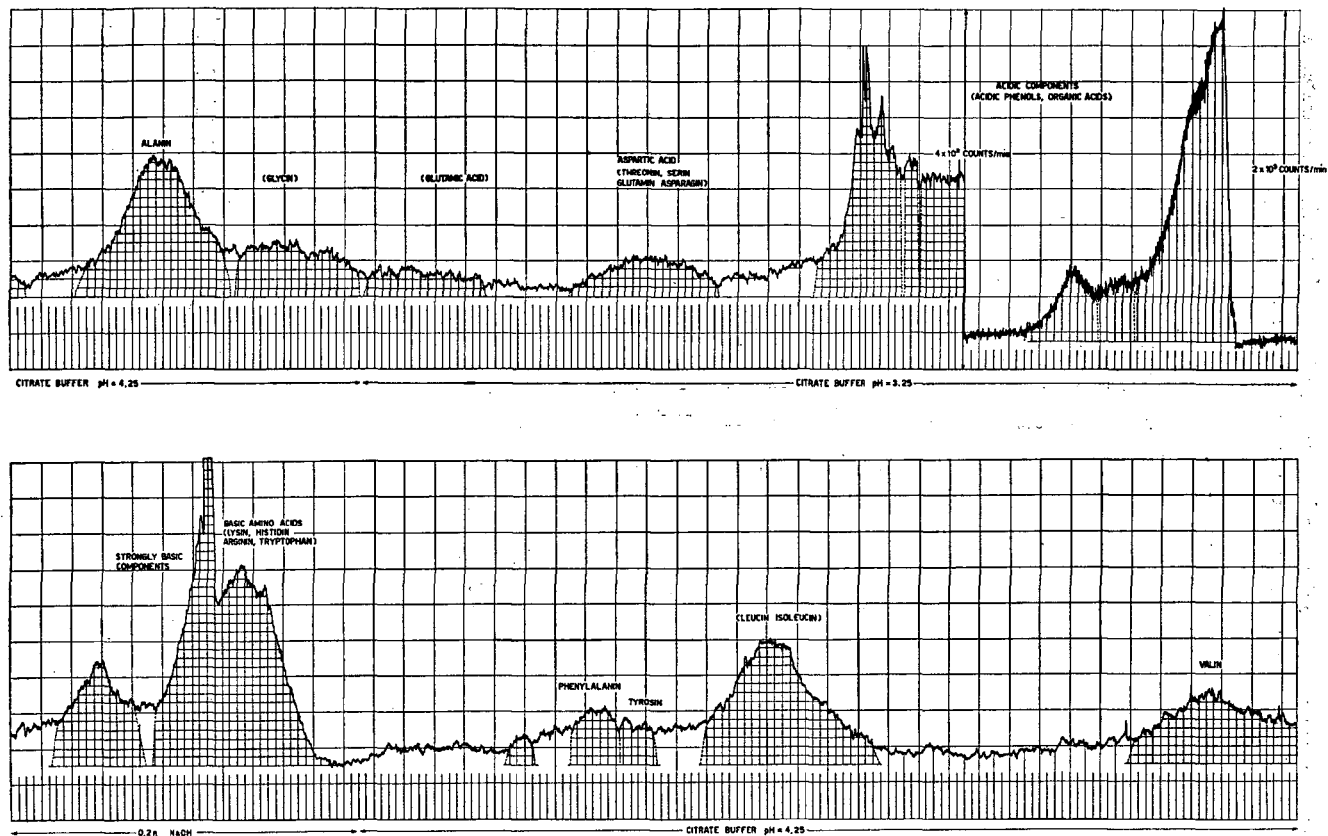


Fig. 12

Flow diagram of H<sup>3</sup>-humic acid hydrolysed in 5 N HCl. Activity test during passage of aqueous column effluent through a bent glass tube with anthracene + POPOP (9:1).

In Fig. 14 the curves of A and B are plotted together and compared with an activity curve obtained by individual methane proportional counting of the effluent samples in the fraction collector. Furthermore, the individual fractions are subjected to quantitative Ninhydrin tests for their amino acid content, following the

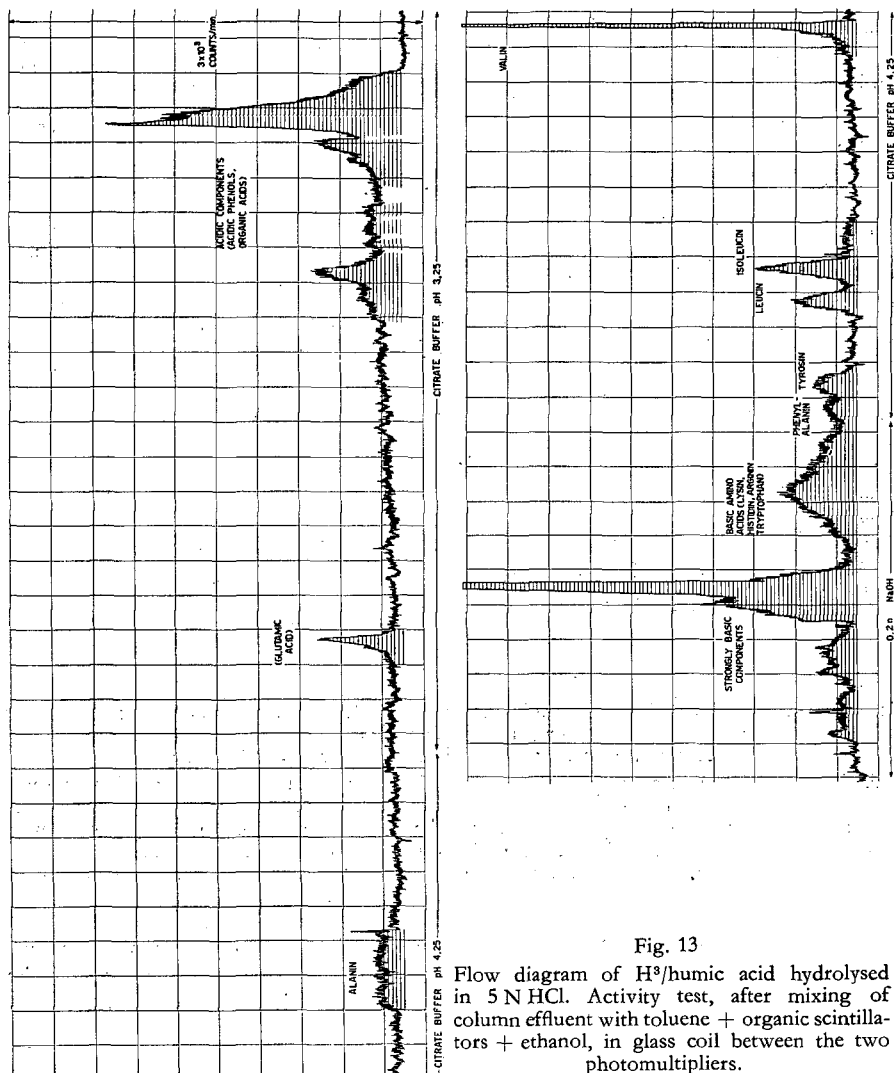


Fig. 13

Flow diagram of  $H^3$ /humic acid hydrolysed in 5 N HCl. Activity test, after mixing of column effluent with toluene + organic scintillators + ethanol, in glass coil between the two photomultipliers.

spot method by MENKE [29]. Thus, this latter curve of Ninhydrin colour intensity shows the peaks of the different amino acids corresponding with those of the flow diagrams. (Experiments A and B.) Some further identification was done on paper with  $FeCl_3$ , ammoniumvanadate and Ehrlich-reagent.

C. ANOTHER FLOW DIAGRAM OBTAINED FROM 5 N HCl HYDROLYSATE OF  $H^3$ -LABELLED PLANT MATERIAL IN THE ANTHRACENE/POPOP TUBE (FIG. 15)

Since this material contains a fair amount of amino acids, a more distinct flow diagram is obtained. Fig. 16 also combines the flow diagram with a curve of in-

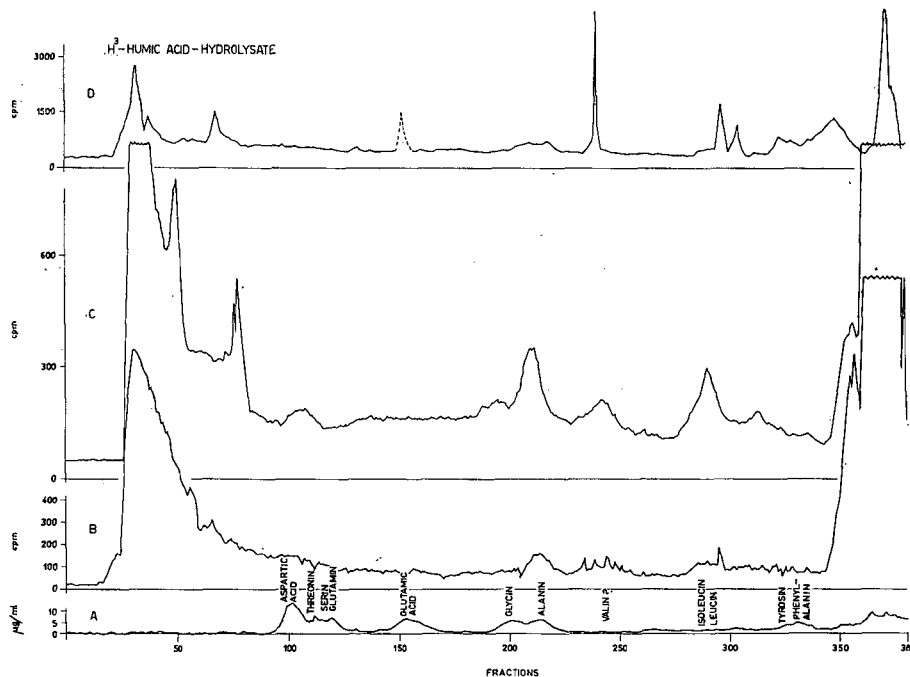


Fig. 14

Flow diagram of  $H^3$ -labelled grass, hydrolysed in 5 N HCl. Activity test during passage of aqueous column effluent through a bent glass tube with anthracene + POPOP (9:1).

Radio column chromatography of  $H^3$ -labelled humic acid hydrolysate.

A Amino acids in  $\mu$ g Leucin equivalents/ml. B Radioactivity measured by windowless proportional flow counting of the individual fractions evaporated in planchets. C Flow counting diagram of column effluent in the liquid scintillation spectrometer (bent glass tube filled with anthracene and POPOP, 9:1). D Flow counting diagram of column effluent in the liquid scintillation spectrometer (glass coil after previous mixing of column effluent 1:30 with toluene + ethanol + DPO + POPOP).

dividual fraction counts under the  $CH_4$ -flow counter and the Ninhydrin-colour curve. Again representative fractions of the peaks were further elaborated on the paper.

## Discussion

With aqueous  $H^3$ -labelled samples, direct recording of the activity, while the column effluent passes through a tube with anthracene + POPOP scintillator, appears preferable to previous mixing of the aqueous effluent with toluene + ethanol + organic scintillators. This becomes evident despite potentially higher yields from toluene + ethanol, for simple economic reasons. Besides, if the aqueous column effluent contains dissolved salts, these often crystallize out in the ternary



toluene-ethanol-water system. When the column separation is a more lengthy procedure, the crystals accumulate and block the solvent flow, thus disturbing the performance. On the other hand, the toluene-ethanol-water system stands freezing temperatures and gives a more favourable background characteristic with practically

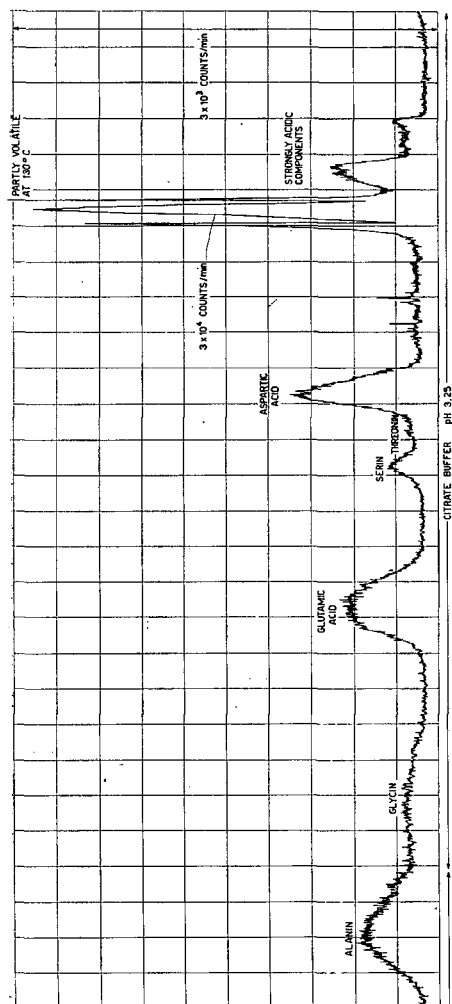
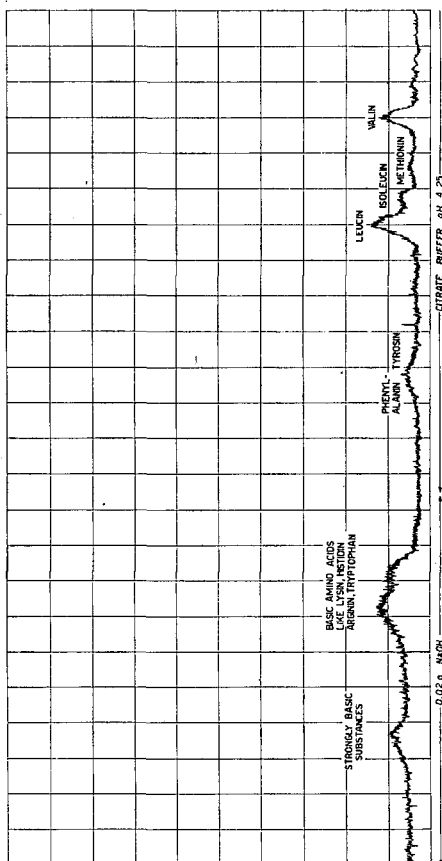


Fig. 15

Flow diagram of hydrolysed  $H^3$ -plant material compared with activity curve of individual fraction counts ( $CH_4$ -flow counter) and Ninhydrin-amino-acid-curve.



no memory effect. In case of organic column effluents which would dissolve the anthracene + POPOP scintillator, the mixing procedure with a subsequent activity test in a glass coil remains the method choice and is economically more realistic, because the mixing ratio can be much narrower.

The anthracene + POPOP-filled bent glass tube, on the other hand, can be cooled down to approximately  $-3^{\circ}C$  when a dosis pump transports the aqueous buffer by soft strokes, thus counteracting the freezing of the water, and when the column

has been thermostatically heated up. Also in the anthracene/POPOP tube the memory effect turned out to be unexpectedly low; the addition of some detergent (e. g. 1 ml/100 ml buffer of Brij 35 = Polyethylenglycolether-solution) might have favoured this.

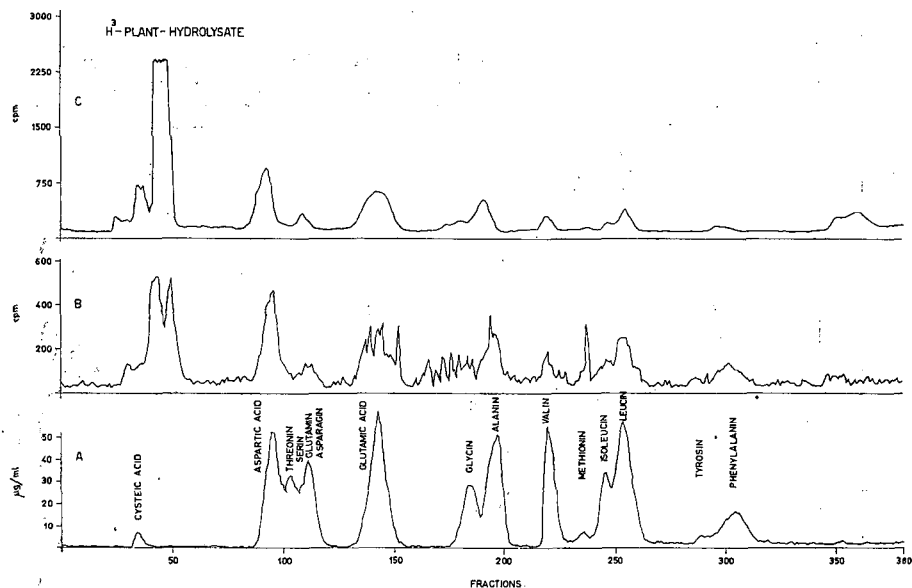


Fig. 16

Flow diagram of hydrolysed  $H^3$ -plant substance compared with activity curve of individual fraction counts ( $CH_4$ -flow counter) and Ninhydrin-amino acid-curve.

Radio column chromatography of  $H^3$ -labelled plant hydrolysate.

A Amino acids in  $\mu g$  Leucin equivalents/ml. B Radioactivity measured by windowless proportional flow counting of the individual fractions evaporated in planchets. C Flow counting diagram of column effluent in the liquid scintillation spectrometer (bent glass tube filled with anthracene + POPOP, 9:1).

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## DISCUSSION XVIII

**P. Springell** (Australia): It seems to me that dilution of the effluent with a liquid scintillator before collection on the turntable may result in excessive dilution for chemical estimation or subsequent recovery of the eluate. Would it not be better to channel part of the effluent directly to the fraction collector? I would also like to know what effect the scintillator has on the Ninhydrin reaction.

**H. W. Scharpenseel** (Federal Republic of Germany): One of the procedures we also considered was this possibility of splitting the column effluent in two parts, channelling one part into the fraction collector and the other, after mixing with toluene and ethanol, into the optical chamber of the Tri Carb equipment. However, we did not use it. As regards the effect of the scintillator on the Ninhydrin procedure, this reaction was carried out with the aqueous column effluent which we obtained after passage through the bent glass tube with POPOP and anthracene. We did not apply the Ninhydrin reaction directly to the ternary system of column effluents plus toluene plus ethanol. However, it is very difficult to get the scintillator out by column chromatography. This great difficulty in getting the column effluent cleaned up again is a further argument against the previous mixing system.

**K. H. Menke** (Federal Republic of Germany): I am the co-author of the above paper. In connection with Mr. Springell's question, I might add that the solid scintillator is totally insoluble in water, so that we did not find any effect on the colour yield in the Ninhydrin procedure. We did the amino-acid estimation by means of spot tests, for which only 1% of the 1.8 ml fraction of effluent is required. This is put on paper and evaluated at two different wavelengths. (The remaining 99% is available for radioactivity measurements.) By this method, we can have three curves from one run with one sample.

**K. H. Kimbel** (Federal Republic of Germany): I would like to ask Dr. Scharpenseel whether the calculation of the counting efficiency was based on equal volumes of effluent. The plastic scintillator tube technique, which was first pro-

posed by Willenbrink and myself three years ago, has been improved in that a tube with an inner diameter of 0.3 mm is now available; flat helices can now be wound from this material and be imbedded in a plastic material, so that the surface/volume ratio of the solution to be counted can be improved considerably.

**H. W. Scharpenseel:** We knew that various brands of scintillator tube having diameters of less than 0.7 mm are now on the market. However, the company from which we ordered such tubes went into liquidation, so that we unfortunately had no practical experience on the subject.

**E. Schram (Belgium):** As Dr. Scharpenseel has just said, the addition of a liquid scintillator to aqueous chromatographic effluents containing salts has a number of drawbacks (immiscibility, high cost, impossibility of subsequent chemical analysis). It was for these reasons that we developed an anthracene powder cell which can be used in conjunction with an automatic amino-acid counter. An initial communication on this subject appeared last year (E. SCHRAM and R. LOMBAERT, *Arch. int. physiol. et biochim.* **68** (1960) 845. The yield for this cell is 2% in the case of tritium having a background of 60 counts/min at room temperature (E. SCHRAM and R. LOMBAERT, *Anal. Biochem.*, in press). With a cell volume of 1 ml, absolute number of counts seems to us to be at least equal to that which can be obtained by means of liquid scintillators, by the method described by Dr. Scharpenseel. I am perhaps a bit more optimistic than Dr. Scharpenseel as regards the superiority of anthracene crystals over liquid scintillators. I should like to ask Dr. Scharpenseel what background he obtained in his recordings and also whether quenching can be regarded as constant during this recording.

**H. W. Scharpenseel:** The background amounts to approximately 80 to 90 counts/min; in the case of the direct counting of the aqueous column effluent, it is 150 or even a little higher. As far as the quenching is concerned, it is unfortunately necessary, in quantitative evaluations, to purify each of the various individual fractions very carefully and to determine the specific quenching characteristics by internal standard methods.

**J. Sharpe:** In Metrology of Radionuclides, IAEA, Vienna, 1960, Dr. Forte of Ispera described a method for the tritium counting of aqueous solutions based on the use of a zinc sulphide phosphor as a scintillator. He used the time correlation of the decay from the zinc sulphide to obtain a low background. I wonder whether Dr. Scharpenseel has considered this possibility in his column work.

**H. W. Scharpenseel:** I have not, but I am very grateful for the suggestion.

# A NEW METHOD FOR MEASURING LOW LEVEL TRITIUM USING A BENZENE LIQUID SCINTILLATOR

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Abstract — Résumé — Аннотация — Resumen

**A new method for measuring low-level tritium using a benzene liquid scintillator.** The tritium activity of rain and free hydrogen may be determined by converting the samples to benzene and counting in a liquid scintillation counter equipped with coincidence and cooling. The water to be measured (the hydrogen samples can be easily and quantitatively converted to water) is added to commercial calcium carbide and acetylene collected. This gas is led into a glass circuit containing a quartz tube heated to 600°C, two traps cooled to dry-ice temperatures, and an all-glass circulating pump. The acetylene polymerizes to a variety of products which are removed continuously by the traps. After virtually all of the acetylene has reacted, the benzene in the traps is separated by distillation. The benzene is then purified by extractions.

Naphthalene is added to the benzene to reduce the freezing point. The present arrangement, which utilizes a counting container of 20 ml, permits 1.2 g of hydrogen to be counted with a background of 25 cpm. The detection efficiency is 35%. Due to the large quantity of hydrogen exposed to the counter, it is possible to measure atmospheric samples without the necessity of isotopic enrichment.

**Nouvelle méthode pour la mesure de faibles teneurs en tritium à l'aide d'un scintillateur liquide au benzène.** Les très faibles teneurs en tritium telles que celles des eaux de pluie et de l'hydrogène libre de l'atmosphère peuvent être déterminées en effectuant la synthèse du benzène à partir de l'hydrogène de l'échantillon.

Le benzène obtenu est utilisé comme solvant dans un scintillateur liquide. La mesure est effectuée à l'aide de deux photomultiplicateurs en coïncidence et refroidis.

L'eau à doser est ajoutée à du carbure de calcium commercial; l'acétylène dégagé est entraîné à l'aide d'une pompe à circulation à travers un circuit comprenant un tube de quartz chauffé à 600°C et deux pièges maintenus à -80°C environ. Les produits de polymérisation obtenus sont retenus dans ces pièges. Lorsque tout l'acétylène est transformé, le benzène recueilli dans les pièges est séparé par distillation; il est alors purifié par extraction.

On ajoute du naphthalène au benzène pour abaisser son point de congélation. Le dispositif présent, qui utilise un scintillateur de 20 cm<sup>3</sup>, permet d'introduire 1,2 g d'hydrogène provenant de l'échantillon, avec un bruit de fond de 25 cpm. Le rendement de détection est 35%.

Ces performances rendent possible la mesure d'échantillons d'eau atmosphérique actuelle, sans enrichissement préalable.

**Новый метод измерения незначительного содержания трития с помощью жидкого бензольного сцинтиллятора.** Незначительное содержание трития в дождевой воде и в свободном водороде атмосферы может быть определено при помощи синтеза бензола на основании пробного водорода.

Полученный бензол используется в качестве раствора в жидком сцинтилляторе. Измерение ведется с помощью двух охлаждаемых фотоумножителей совпадений.

Вода добавляется к промышленному карбиду кальция; освобожденный ацетилен с помощью циркуляционного насоса пропускается через цепь с квартовой трубкой нагретой до 600°C, и через две ловушки с температурой около -80°C. Полученные продукты полимеризации задерживаются в этих ловушках. Когда весь ацетилен трансформирован, бензол, собранный в ловушках, отделяется путем дистилляции; затем он экстрahируется.

Для понижения точки замерзания к бензолу прибавляется нафталин. Настоящий прибор, использующий сцинтиллятор в 20 см<sup>2</sup> позволяет ввести 1,2 гр водорода, взятого из пробы с фоном в 25 отсчетов в минуту. Эффективность обнаружения равна 35 %.

Эти результаты делают возможным измерение проб атмосферной воды без предварительного обогащения ее.

**Nuevo método para medir bajas concentraciones de tritio utilizando benceno como solvente del centelleador.** La actividad del tritio contenido en el agua de lluvia y en el hidrógeno atmosférico libre puede determinarse convirtiendo las muestras en benceno y efectuando el recuento con un contador de centelleador líquido, provisto de un dispositivo de coincidencias y de refrigeración. El agua cuya actividad se desea medir (las muestras de hidrógeno pueden transformarse fácil y cuantitativamente en agua) se hace reaccionar con carburo cálcico comercial, con lo que se obtiene acetileno. Este gas se hace pasar por un circuito de vidrio que comprende un tubo de cuarzo calentado a 600°C, dos trampas refrigeradas mediante hielo seco y una bomba de circulación, totalmente de vidrio. Por polimerización, el acetileno forma diversos productos que son separados continuamente por medio de las trampas colectoras. Cuando la totalidad del acetileno ha reaccionado, el benceno acumulado en las trampas se separa por destilación, para purificarse seguidamente por extracción.

Al benceno se añade naftaleno para reducir su punto de congelación. Con el sistema actual, provisto de un depósito de 20 ml, se puede efectuar el recuento de 1,2 g de hidrógeno con una actividad de fondo de 25 impulsos por minuto. El rendimiento de detección alcanza a un 35%. Debido a la gran cantidad de hidrógeno que queda expuesta al contador, es posible medir muestras tomadas de la atmósfera sin necesidad de proceder a un enriquecimiento isotópico previo.

## Introduction

Tritium occurs on the earth in relatively large quantities because of the comparatively high cross section for its production by nuclear interactions of cosmic rays on atmospheric oxygen and nitrogen and, more recently, as a result of the nuclear fusion bombs that have been tested in various locations throughout the world. However, the rapid mixing of this isotope with the extensive amounts of water and hydrogen gas existing in the atmosphere leads to samples of quite low specific activity. This fact, coupled with that of the very low-energy beta disintegration of tritium, particularly disadvantageous for efficient detection, renders precise measurements of naturally-occurring tritium fairly difficult. Nevertheless, the problem has been effectively solved by the use of a preliminary isotopic enrichment step, which, concentrating the heavy isotope into samples of higher specific activity, permits activity determinations by the standard methods of low-level counting.

The rapid increase of tritium in the atmosphere over the past few years has brought its concentration to a point where it is just below the limit of sensitivity, without enrichment, of present standard techniques. It would seem useful, therefore, to develop a method with a little more sensitivity than those in use at this time. The procedure would permit the monitoring of tritium in rain to be made without the troublesome step of enrichment. Moreover, tracer studies in biology and hydrology which habitually require the counting of low specific activity samples would profit by a significant increase in detection sensitivity.

The method described in this paper substantially increases the intrinsic sensitivity of low-level tritium measurements by employing a system which counts larger quantities of hydrogen than hitherto available. It involves a modification of a

procedure for radiocarbon dating that is at present being developed in our laboratory [1]. Fig. 1 shows a synopsis of the chemical procedure.

In essence, benzene is completely synthesized from the water sample whose tritium content is to be measured. The benzene, after purification, is counted in

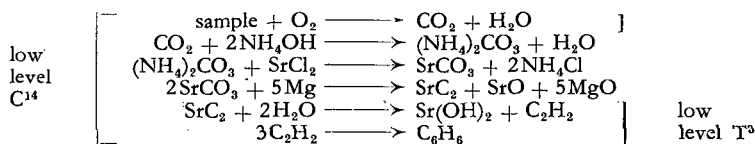


Fig. 1

Chemical reactions of the benzene method for low level radiocarbon and tritium measurements.

a liquid scintillation counter. The chemistry necessary for tritium is much simpler than that involved in  $C^{14}$ -dating as the alkali metal carbide used for the production of acetylene may be purchased from commercial sources. Actually  $CaC_2$  was used here. The carbon in this compound has its origin in coal and, therefore, shows no contaminating radiocarbon activity. The elimination of the necessity for the preparation of carbide in each measurement represents a large saving of time over the  $C^{14}$ -dating procedure, as this step is by far the most difficult. As will be shown in the next section, the polymerization of acetylene to benzene is carried out smoothly and with little trouble.

### Sample preparation

Samples not in the form of water are burned in an oxygen stream and the water collected quantitatively in a cooled trap. This step is a standard procedure of organic analysis. However, the majority of samples submitted for tritium content determination are already in the form of this liquid and need not be further treated

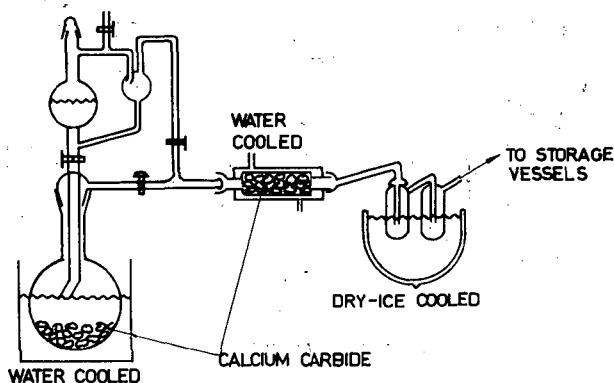


Fig. 2

Acetylene generator.

before use in the acetylene generator. Even ordinary rain samples containing carbon dust, dissolved carbon dioxide, and inorganic salts (but not ammonia) may be used directly without preliminary distillation.

The apparatus employed for the conversion of water to acetylene is shown in Fig. 2. On the far left is the device permitting the drop-wise addition of the water

sample to commercial grade calcium carbide in a 500 cm<sup>3</sup> evacuated flask. The arrangement of stop-cocks facilitates the preliminary separate evacuation of the water and carbide containing parts. As the reaction is exothermic, the bottom flask is water-cooled during the operation. This flask is turned from time to time to allow a more even attack of the carbide. In our laboratory, the standard procedure was to use 150 cm<sup>3</sup> of water and a large excess of carbide.

Following this generator is a water-cooled tube containing small pieces of carbide intended to dry the gas by reacting with the water that is swept over in the acetylene stream. Connected to this is a double trap which removes the small amount of water remaining and a variety of other impurities. The acetylene is then collected in evacuated storage vessels. At least 99.5% of this gas may be frozen out with a liquid nitrogen-cooled trap, which indicates that the system is essentially free from oxygen, hydrogen, and nitrogen.

Due to the rapid formation of the hydroxide from calcium oxide, 50% of the water added cannot be converted into acetylene. In addition, various amounts are lost on the walls and in wetting the hydroxide powder. The acetylene generation as employed in our system produced two moles of this gas in one to two hours. As a result of the rapid production there was a yield of approximately 30%. This could be improved by a larger excess of carbide in small pieces continuously stirred and the water added slowly. However, the limit would be 50%. It will be explained in the last section why it was decided not to strive for this maximum yield.

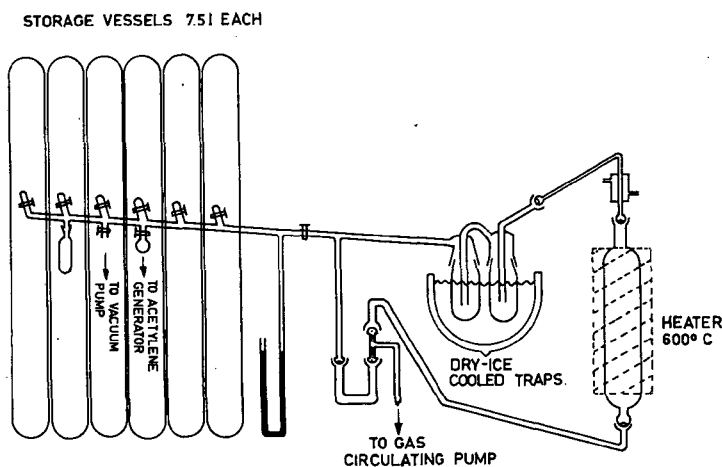


Fig. 3

Acetylene to benzene system.

Fig. 3 shows the vacuum rack for the production of benzene. The apparatus is evacuated and the acetylene produced by the device of Fig. 2 is led into the storage vessels. The usual procedure was to fill all of these containers to just under one atmosphere. After this filling was completed the stopcock connecting the storage half of the system to the polymerization half (the stopcock furthest to the right in the diagram) was opened. The gas circulating pump was started, the double trap system cooled by a dry ice mixture, and the furnace brought to its optimum



temperature of 600 °C in about 20 min. At this temperature a homogeneous reaction of the second order produced benzene with a yield, in this arrangement, of 40—50%. The heated tube was of quartz, 40 cm long and with an internal diameter of 4.5 cm. The circulating pump had a delivery which enabled a molecule of the gas to pass through the heated tube in the order of one minute [2]. The reaction proceeded at a moderate rate and was completely under control with no catalyst in the tube. The benzene and other hydrocarbon products were continuously frozen out in the cooled traps. The acetylene that had not reacted was passed through the tube again by the circulating pump.

As the acetylene reacted and the products were removed by the traps, the pressure in the system dropped. Gas from the storage vessels was continuously being added to that in the circuit to slow down the pressure decrease, but was not circulating through the heated tube while it was being stored. In practice, the reaction was usually started toward the end of the day and run throughout the night without adjustment. The next morning it was found that approximately one half of the acetylene, i. e. one mole, had reacted. The reaction proceeded slowly at this time for two reasons: firstly, the polymerization of acetylene to benzene is bimolecular and the reaction rate decreased rapidly with pressure and, secondly, some of the side reactions produced hydrogen gas which stayed for the most part in the circuit half of the apparatus and, therefore, diluted the acetylene in the reaction tube. To increase the pressure, the gas was frozen out (in several steps) of two or three of the storage vessels and then allowed to pass into some of the half-filled containers. Liquid nitrogen and the vertical tube seen on the far left of the diagram were used for this purpose. The gas in the circuit half was then expanded into one of the empty storage bulbs and the acetylene separated from the hydrogen with liquid nitrogen.

The reaction was carried on for another day and night, the acetylene pressure being maintained by concentration into only two and at last a single storage vessel. At the end of the second day 95% of the gas had reacted.

The liquid collected in the traps was removed and submitted to a gross distillation which separated the products coming over at 60° to 90 °C and quantitatively collected the impure benzene. The slightly yellow liquid was then submitted to several extractions to remove the more difficult impurities. In the present work with tritium dosage, the principal material that contaminated our benzene was thiophene, a heterocyclic sulphur compound that was readily formed by the action of hydrogen sulphide with acetylene. The type of carbide commercially available in France is severely contaminated by sulphides. Thiophene, having almost the same boiling point as benzene and being chemically similar, cannot be separated by an ordinary fractional distillation or the usual size columns of gas phase chromatography. However, it may quickly and easily be extracted by concentrated sulphuric acid and in order to acquire the pure benzene, it was necessary to carry out this process.

The other quenching impurities in the benzene are mostly amines and may be extracted with a dilute acid solution. After this, distilled water extractions rid the system of inorganic ions and extract any organic acids or aldehydes that are present. After the water is drawn off, the benzene is dried with a small amount of dehydrated sodium sulphate. The careful use of a 40 cm Vigreux distillation column provides the final purification. The next stage is to clean out any dissolved oxygen with argon and the phosphors and naphthalene may then be added. The usability of the solution is verified by observation of the spectrum shown by an

external  $\text{Cs}^{137}$  gamma source which is then compared with the spectrum obtained using a purified commercial benzene solution. If the positions of the spectra are identical, the solution to be measured is verified as being free from seriously quenching impurities. Half an hour is required for the extractions using only a simple laboratory separatory funnel. The entire purification procedure lasts approximately two hours. Unfortunately, the exchange of the hydrogens of the benzene with those of concentrated sulphuric acid is rapid [3] and for this reason it is necessary to use a commercial carbide without the large quantity of sulphides found in the French variety. As a last resort, we can produce our own carbide from sulphur-free carbon. The exchange between benzene and dilute sulphuric acid is very slow and should be negligible for the step of the extraction of the amine impurities.

### Counting system

To 18 cm<sup>3</sup> of the pure benzene is added 2.2 g naphthalene together with quantities of PPO and POPOP to provide concentrations of 4 g/l and 0.1 g/l, respectively. The naphthalene is primarily intended to lower the freezing point of the benzene, but also serves the useful purpose of reducing the quenching power of impurities in the solution [4]. Naphthalene, when available commercially, is a product of coal tars and therefore shows no radiocarbon or tritium activity.

The counting container was a cylindrical quartz vessel, with an internal thickness of 2.4 cm while the internal diameter of the faces measured 4 cm. The side wall of this container was silvered for light reflection. Two selected photomultipliers view the solution through optical joints of silicon oil. The use of pulse coincidence electronic circuits to reduce noise originating in the photomultipliers is now a standard procedure in the liquid scintillation counting of tritium and need not be discussed here. The details of the actual instrument used in this work have been published [5].

Cooling of the photomultipliers and counting vessel to 0°C (just above the freezing point of the solution) and moderate shielding with lead reduces the background to 25 cpm with a detection band allowing 35% disintegration detection efficiency.

### Discussion and evaluation

This synthesis of benzene as described above is now carried out routinely in our laboratory and causes no difficulty. The total chemical yield, for the purpose of tritium counting, is of the order of 10%. There seems little hope of a significant increase as the limiting yield of the attack of the carbide with water is in theory 50%. Over a year's experiments with variables in the acetylene to benzene reaction have taken place but the possibility of obtaining more than 50% without making use of difficult catalysts that do not lend themselves to routine treatment seems remote. It must be realized that small losses in transferring operations are unavoidable and a practical limit of 20% to the chemical yield might be set. The higher yield of 30% realized in the use of the method for  $\text{C}^{14}$ -dating is due to the acetylene generation step giving a yield of 100% when determined relative to the carbide. It is the isotope in the latter which is of interest in this case.

Nevertheless, the low chemical yield has not been of major concern to us since the water specimens for which we developed the method are all of large quantity.

This particularly applies to experiments on samples in the science of hydrology and meteorology. The minimum amount of water necessary for effective measurement in the present arrangement is of the order of 100 ml. This is even not considered excessive for many aspects of biological research.

It is difficult to specify exactly the work involved in this method; an estimation would be one man-day (8 h) of actual work for each sample. With only one vacuum line as shown in Fig. 3, two samples could be run each week. The work involved seems fairly comparable to that of the standard arrangements necessitating preliminary isotopic enrichments. Also, the equipment necessary for the method described here is no more extensive than that of the arrangements requiring enrichments.

TABLE I

## COMPARISON OF SOME LOW-LEVEL TRITIUM COUNTING SYSTEMS

The terms in the figure of merit, column 3, are  $g\ H = g$  of hydrogen counted that have an origin in the sample being measured,  $\%$  = per cent efficiency of the counter, and  $\sqrt{bkg}$  = square root of the background in counts/min.

System	Reference	$\frac{g\ H \times \%}{\sqrt{bkg}}$	Enrichment necessary to obtain statistics comparable to those of the benzene scintillator
H <sub>2</sub> gas counting, anticoincidence ring	[6]	1	8
H <sub>2</sub> gas counting, anticoincidence ring	[7]	0.26	32
5% water in a Kinard scintillator, liquid scintillation counter	[5]	0.72	12
Benzene in a liquid scintillation counter	[this work]	8.4	—

In Table I a comparison has been made with some standard procedures described in the literature [5—7]. The figure of merit was chosen as:

$$\frac{g \text{ of hydrogen counted} \times \text{counting efficiency in } \%}{\sqrt{\text{background}}}$$

This seems to be indicative of the sensitivity of the existing methods. It may be seen in the last column that the procedure described in this paper is intrinsically more sensitive than the others by a factor of ten. That is to say, for a given sample, the other arrangements would need a preliminary enrichment of the water of approximately ten times in order to obtain the same statistics as the benzene scintillator.

The main disadvantage of the benzene method is the low chemical yield as compared to the high efficiency of water enrichment by electrolysis. For this reason the method will be limited to use in studies having samples of at least 100 cm<sup>3</sup> of water. To increase the sensitivity of the present arrangement, two changes might be applied. If the quantity of the sample is sufficient, a preliminary gross enrichment could be effected and the benzene then synthesized from the enriched water. Also, larger size sample containers might be used in the liquid scintillation counter as the additional work necessary for larger quantities of benzene is not at all proportional to the amount of the liquid. For example, to synthesize 80 cm<sup>3</sup> of benzene requires only twice as much actual work as 20 cm<sup>3</sup>.

However, for samples of smaller size the methods described by other scientists

would be better. If the tritium concentration is very low, the high yield of the electrolysis enrichment is a strong advantage. In ordinary tracer studies with samples of high tritium activities, the almost direct usage of water-containing scintillators in the liquid counters is much more simple than carrying out the procedure for the preparation of benzene. Therefore, the benzene scintillator described here will be best used in studies of hydrology and meteorology where the samples are habitually large and of low tritium content.

There are two other methods for the dosage of low-level tritium described by other scientists. A high intrinsic sensitivity may be obtained by visual observations of tracks in a diffusion cloud chamber [8]. Our experience with a cloud chamber of this sort, in connection with another project, leads us to believe that the metastable conditions of this device will never permit routine measurements. A more promising method is one involving the direct transfer of a part of the tritium of a water sample to toluene which is being shaken with the water [9]. Although this paper does not give enough specific information to allow a comparison with the benzene scintillator, the method can be used for routine purposes.

The low chemical yield in the synthesis of benzene has caused concern over isotope effects that should be important due to the large mass difference between hydrogen and tritium. A negative enrichment of 20% of deuterium was derived from the procedure described in this paper as measured by a mass spectrometer. We eventually plan to determine this factor for tritium using a tritiated water sample of known activity, but, at this time, we are reluctant to contaminate the system. The experiment will permit the determination of the ratio of the isotope effects for deuterium and tritium; this means that samples may be submitted to routine mass spectrometer analysis to determine the isotope effect corrections. However, until these measurements are made, we may estimate that the isotope effect for tritium is about double that for deuterium. That is to say, there is, unfortunately, a negative enrichment of about 40% of tritium in this method.

There is reason to believe that since the chemical yield seems to be about the same with each run, the isotope effect will be roughly reproducible. It is conservatively estimated that this will be within plus or minus 25% of the assumed 40% effect. In other words, the isotope effect should be, in each run,  $40\% \pm 10\%$ . If this can be verified as being the case, the routine mass spectrometer analyses of the benzene samples will not be necessary if one is willing to accept an uncertainty of 4% in the tritium concentration measurements, due to variations in the isotope effect. Errors involved in electrolysis enrichment calculations are of at least this order of magnitude. Therefore, the use of the benzene scintillator offers the possibility of the elimination of the need for a deuterium analysis of each sample. This would simplify the work in most laboratories which use the ordinary naturally occurring tritium dosage methods.

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## DISCUSSION XIX

**D. Lal (India):** Have the authors tried to measure the isotopic separation effects which take place in the preparation of benzene?

**M. Tamers (France):** We hope to make this measurement by simply using a standard water sample with a known amount of tritium. At the present time we do not want to contaminate our laboratory, which is a low-level set-up. We have determined the degree of deuterium enrichment. We might say that the tritium enrichment is about twice as great, unfortunately a 40% negative enrichment. These figures are tentative, but I believe that we should be able to measure the separation effect with good reproducibility.

**H. G. Östlund (Sweden):** I would like to ask what amount of water you start out with and secondly, what amount of water equivalent do you have in your counting system cell. Also, what is your standard deviation, in tritium units, after a counting time of, say, 1000 min?

**M. Tamers:** As regards the amount of water equivalent in our sample, we have of the order of 1.25 g of hydrogen being counted so that water equivalent would be  $9 \times 1.25$  or 11 g. This is the equivalent of putting 55% water into the scintillator. Using the 20 ml vial and a 24 h count, which is our standard practice, and on the basis of 2 pi sigma statistics, we will be able to detect activities as low as 9 T.U. For the 80 ml sample vial, the figure is between 3 and 4 T.U.

In answer to the other part of your question, we start out with about 150 ml water.

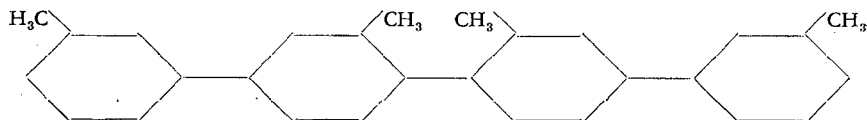
**J. C. Burr (United States of America):** Has the speaker considered the possibility of putting a heated palladium valve at 200–400 °C and connected to a vacuum system on the off-side into his conversion system? By so doing, he could easily, safely, rapidly and continuously pump off the hydrogen during the night and thus prevent the pressure build-up and dilution which slows the conversion reaction.

**M. Tamers:** The amount of hydrogen that is actually in the system overnight is not very great. It might be a few per cent. What we try to do at all times in this work is to keep the system as simple as possible. It would not be worth-while to add the arrangement which has been suggested.

**B. Grinberg (France):** During your process for preparing acetylene, very pronounced isotopic separation takes place and consequently there is a reduction in tritium content. Did you take this isotopic separation into account in your calculation of the final tritium content of the water? It has been our experience, in preparing acetylene under the same conditions, that the H/T ratio differs by about 20–30% from the H/T ratio in the original water.

**M. Tamers:** As I pointed out before, the isotope effect which we observe is also negative and is probably of the order of 40% for tritium. The figure for deuterium is 20%. This will, of course, have to be taken into account in the final calculations.

**N. W. E. Nay (Federal Republic of Germany):** I might inform the speaker that several p-oligophenylenes recently synthesized in our laboratories have been tested by us as solutes for liquid scintillators. The  $1^22^33^24^3$  tetra-methyl-p-quaterphenyl



has the advantage of a higher relative pulse height (1.17) and of better solubility in toluene than PPO. The counting efficiency of this primary solute with POPOP as a wave-length shifter is 35.4% for toluene soluble tritium (instead of 27.5% with PPO and POPOP). The synthesis of this compound is quite easy and its cost is only about 25% that of PPO.

**E. A. Evans** (United Kingdom): Has Dr. Tamers considered the possibility of using a catalyst, such as nickel carbonyl, to speed up the conversion of the acetylene to benzene?

**M. Tamers:** We have looked into the possibilities of catalysts. The chemical yield of the simple ones is no better than the yield we have already obtained, i. e. 40–50%. Some catalysts mentioned in the literature seem very good, but unfortunately they are all dangerous. Our system is intended as a routine method and we simply do not feel that we can use difficult catalysts.

**J. L. Garnett** (Australia): In connection with the references during this discussion to the use of transition metal catalysts, e. g. palladium, for enhancing the conversion of acetylene to benzene, we have observed in our work that care must be exercised in procedures of this type because extensive catalytic exchange is likely to occur under these conditions and a finite isotope effect can also be expected.

# DIRECT MEASUREMENT OF TRITIUM IN BIOLOGICAL MATERIALS WITH THE LIQUID SCINTILLATION COUNTER

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Abstract — Résumé — Аннотация — Resumen

**Direct measurement of tritium in biological materials with the liquid scintillation counter.** Procedures for measurement of tritium in animal tissues and isolated tissue fractions have been reported in the literature. In all the work reported, however, a liquid scintillation coincidence spectrometer has been used for the counting of the samples. In this work a single phototube liquid scintillation counter was used for the measurements.

Investigation centred primarily on the direct dissolution of animal tissue in Hyamine 10-X and the suspension counting of lyophilized tissue in scintillating gels. Different tissues, such as liver, intestine, blood and skin, can be dissolved directly in Hyamine and measured with an efficiency of 10–15%.

The techniques of quenching correction and certain phosphorescence phenomena as they affect the counting in a single phototube counting system are discussed.

The sensitivity of the method, although somewhat less than that of the coincidence-counting arrangement, seems to be sufficient for many applications.

The work reported was carried out on tissue samples from mice previously injected with tritium-labelled thymidine. When a dose of approximately 1  $\mu\text{C}$  tritiated thymidine per g of body weight was injected into the mice, the metabolic fate of the thymidine incorporated into deoxyribonucleic acid (DNA) of the various tissues could be followed for a period of one month.

**Détermination quantitative directe du tritium dans les substances biologiques, au moyen de compteurs à scintillations à liquides.** Diverses techniques de détermination du tritium dans les tissus animaux et fractions isolées de tissus animaux ont déjà été décrites. Mais toutes comportent l'emploi d'un spectromètre de coïncidences à scintillations à liquides pour le comptage des échantillons. Pour faire cette détermination, l'auteur s'est servi d'un seul phototube-compteur à scintillations à liquides.

Il a étudié surtout la dissolution directe de tissu animal dans de l'hyamine 10-X, et le comptage de tissus lyophilisés en suspension dans des gels à scintillations. Certains tissus, tels que le foie, l'intestin, le sang et la peau, peuvent être dissous directement dans l'hyamine et le rendement de la détection peut être de 10 à 15%.

L'auteur examine les techniques de correction de coupage et certains phénomènes de phosphorescence dans la mesure où ils ont une influence sur le dispositif de comptage à un seul phototube.

Cette méthode, bien que moins précise que le dispositif de coïncidence, l'est suffisamment pour de nombreuses applications.

L'expérience qui fait l'objet du mémoire a porté sur des échantillons de tissus de souris auxquelles on avait injecté au préalable de la thymidine marquée au tritium. Lorsqu'une dose d'environ 1  $\mu\text{C}$  de thymidine tritiée par gramme de poids du corps est injectée aux souris, on peut suivre pendant un mois les transformations métaboliques de la thymidine incorporée à l'acide déoxyribonucléique (ADN) des divers tissus.

**Непосредственное измерение количества трития в биологических материалах при помощи жидкого сцинтилляционного счетчика.** В литературе уже сообщалось о способах измерения количества трития в тканях животных и в изолированных срезах тканей. Однако при всех описываемых работах для отсчета импульсов образцов применялся жидкостный сцинтилляционный спектрометр совпадений.

При выполнении настоящей работы для измерений был использован жидкостный сцинтилляционный счетчик с одним фотоэлементом.

Исследовались главным образом непосредственное растворение тканей животных в гиамине 10-X и отсчет импульсов взвеси лиофилизованной ткани в сцинтиллирующих гелях. Различные ткани, как например, печень, кишечник, кровь и кожа могут быть непосредственно растворены в гиамине и активность их измерена с точностью до 10—15 процентов.

Будут обсуждены методы введения поправки на гашение и некоторые явления фосфоресценции, поскольку они влияют на отсчет импульсов в счетном устройстве с единым фотоэлементом.

Хотя чувствительность этого метода представляется несколько меньшей, чем при использовании счетчика совпадений, однако этот метод удовлетворителен для многих видов применений.

Представляемая работа была проведена на образцах тканей мыши после предварительной инъекции меченого тритием тимидина. При впрыскивании в мышь дозы приблизительно в 1 микрокюри тритированного тимидина на грамм веса ее тела, метаболическая судьба тимидина, поглощенного дезоксирибонуклеиновой кислотой различных тканей, могла быть прослежена в течение целого месяца.

**Determinación cuantitativa directa del tritio en sustancias biológicas mediante contadores de centelleador líquido.** Ya se han presentado informes acerca de los procedimientos aplicados para la determinación cuantitativa del tritio en tejidos animales y fracciones aisladas de los mismos. Sin embargo, en los trabajos respectivos se han utilizado siempre, para el recuento de la muestra, espectrómetros de coincidencia de centelleador líquido. En cambio, en el presente trabajo las mediciones se han efectuado con un contador de centelleador líquido equipado con un fototubo único.

Se investigó principalmente la disolución directa de tejido animal en la hiamina 10-X y el recuento del tejido liofilizado en suspensión en geles de centelleo. Es posible disolver directamente en hiamina tejidos diferentes tales como el hepático, el intestinal, el sanguíneo y el cutáneo, y medirlos con un rendimiento de 10 a 15%.

El autor examina la técnica aplicada para la corrección por extinción, así como ciertos fenómenos de fosforescencia que afectan la determinación en el sistema de recuento de fototubo único.

Parece que el método ofrece una sensibilidad suficiente para muchas aplicaciones, aunque un poco menor que la del dispositivo de recuento por coincidencias.

La labor de que se informa se llevó a cabo con muestras de tejidos de ratón a los que se había inyectado previamente timidina marcada con tritio. Después de inyectar al ratón una dosis del orden de 1  $\mu$ c de timidina tritiada por gramo de peso corporal, se pudieron seguir durante un mes las transformaciones metabólicas de la timidina incorporada al ácido desoxirribonucleico (DNA) de los distintos tejidos.

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## Introduction

The availability of tritium-labelled compounds at high specific activities has increased their application as biological tracers. Tritium-labelled organic compounds are widely used for the study of biological processes and metabolic pathways. A radiochemical method for the quantitative determination of tritium in whole animal tissue and tissue fractions is therefore of great interest.

Liquid scintillation counting offers a rapid and sensitive method for measuring low-energy beta-emitters. It therefore appears to be the preferable method for a relatively simple and reliable technique of direct measurement of tritium in biological materials.

The determination of tritium in animal tissue has been reported earlier [1, 2].



In all the work reported, however, a liquid scintillation coincidence spectrometer has been used for the counting of the samples.

In this work a single phototube liquid scintillation counter was used for the measurements. The purpose of the present work is investigation of the sensitivity and reproducibility which can be achieved with this counter.

One of the chief difficulties in liquid scintillation counting of tissues is the great quenching effect due to the coloured solutions formed when tissues are dissolved. A method of quenching correction by measurement of the colour intensity of the solutions will be described in this paper.

The work reported here was carried out on tissue samples from mice previously injected with tritium-labelled thymidine.

#### SAMPLE PREPARATION

For liquid scintillation counting it is usually necessary to have the sample in a form soluble in or miscible with the scintillation solution. By use of the quarternary ammonium base Hyamine, *p*-(diisobutyl — cresoxy ethoxy ethyl) dimethyl — benzyl ammonium hydroxide, proteins, amino acids and whole animal tissue can be complexed and brought into solution.

Another possible approach is direct counting of the material as a suspension. The fine dispersed material can be stabilized with a gel and held in a uniform suspension for the extended period of time necessary for counting.

### Experimental

#### COUNTING IN HOMOGENEOUS SOLUTION

The possibility of dissolving animal tissue in Hyamine was first reported by AGRANOFF [3]. Other methods for tissue dissolution have been reported by HERBERG [1], with ethanol-potassium hydroxide, and by KINNORY [2], who found formamide useful in the dissolution of tissues.

Each of these dissolving agents requires a special solvent system for liquid scintillation counting, and the counting efficiency largely depends upon the solvent system used. Because of the low temperature necessary to operate the single phototube liquid scintillation counter for tritium counting, the choice of solvent system is rather restricted.

All three methods of tissue dissolution were examined in the course of this work. Hyamine was found to be the most suitable solvent for various kinds of tissue samples. The tissue digest in Hyamine also possesses the advantage that it is readily miscible with toluene, one of the most efficient solvents for liquid scintillation counting.

#### METHOD OF SAMPLE PREPARATION

An aliquot of the wet or lyophilized tissue is transferred to a small glass vial; in the case of small organs the whole tissue can be transferred directly into the vial.

1 ml of a 1 Molar methanolic solution of Hyamine is added to the sample, and the vial is placed in a water bath at 50–60°C until complete tissue dissolution occurs. The temperature should not exceed 60°C; higher temperature may cause decomposition of the Hyamine and give dark colours.

Almost any type of animal tissue can be dissolved this way; and various tissues, such as liver, blood, intestine, skin and muscle, have been successfully dissolved.

Up to 40 mg of dry tissue sample, or 200 mg of wet tissue, will dissolve in 1 ml of the Hyamine solution. When the tissue is dissolved, the sample is cooled to room temperature and transferred to the weighing bottle, which is used for counting.

A scintillation solution is added to the sample to give a total volume of 20 ml. The scintillation solution consists of 6 g/l PPO, 2.5 diphenyl-oxazole and 0.1 g/l POPOP, 1,4—bis —2 — (—5 phenyloxazolyl) — benzene in toluene. The samples are then cooled in a deep-freezer overnight before being counted in the liquid scintillation counter.

#### COUNTING

A limiting factor in liquid scintillation counting is the high background due to noise pulses from the photocathode. This background may be reduced in two ways: by keeping the photomultiplier at a low temperature or by employing two photomultipliers in a coincidence circuit to eliminate random pulses.

In this work a single phototube liquid scintillation counter, Ecko N 612, was used for counting. The counter was kept at a temperature of  $-20^{\circ}\text{C}$ . An E.M.I. 9514 S photomultiplier was used in the counter. The sensitivity curve of the photomultiplier is in the 300—600 m $\mu$  region with a broad peak at 420 m $\mu$ . Silicon oil was used for optical coupling between the sample vial and the phototube. The optimum operating voltage of the counter was determined with spiked tissue samples. The efficiency of the counter was determined with a tritium-labelled toluene standard.

#### QUENCHING CORRECTION

Tissue samples dissolved in Hyamine have a yellowish colour, the intensity of the colour increasing with increasing amounts of tissue, but differing not too much from one tissue to another, except for blood, which gives a very intense colour. Unfortunately, this yellow solution absorbs some of the light emitted by the phosphor, and the counting efficiency is therefore decreased. This effect is generally referred to as the quenching effect or the absorption effect. A proper correction for the quenching is of greatest importance for reproducible measurement of the tritium activity.

Different methods of quenching correction have been investigated.

##### *1. Internal standard technique*

The internal standard technique involves the addition of a standard amount of activity to all the experimental samples and a recounting. By observation of the ratio of the increment in the counting rate due to the addition of the standards for each sample to the counting rate of the standard alone, the counting rates of the experimental samples can be corrected for quenching and absorption. The internal standard technique, however, involves two counting operations on each sample.

##### *2. Extrapolation technique*

Another method of correcting for quenching without the use of an internal standard is by extrapolation of the observed counts at different sample concentrations to obtain the true specific activity of the sample. This technique may be

useful provided that the quenching is a simple function of the sample concentration.

The quenching properties of tissue samples on the counting efficiency for tritium was therefore investigated more thoroughly.

When a tissue sample containing tritium was counted at the voltage giving maximum counting efficiency, the counting efficiency decreased as an exponential function of the sample concentration, provided that the counting efficiency had been corrected for quenching from the Hyamine solution.

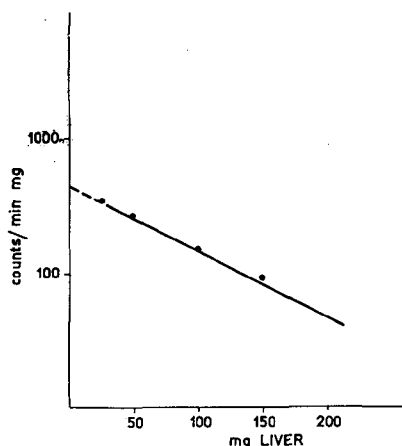


Fig. 1

Specific counting rate as a function of tissue concentration.

Fig. 1 shows the counting rate per mg of a tritium-labelled liver sample decreasing exponentially as a function of the sample concentration. Similar curves have been obtained for samples of other tissues, including lungs, intestine and blood.

The same relationship has been reported by KERR *et al.* [4] for the counting of carbon-14-labelled benzoic acid in the presence of organic compounds giving various degrees of quenching and by C. T. PENG [5] for the counting of sulphur-35-labelled organic compounds. This relationship, however, cannot always be applied when the quenching correction for tritium counting is concerned. Quenching curves for tritium counting are usually characterized by a rapid decrease in counting efficiency when only small amounts of quenching material are added. When a certain concentration has been reached, the decrease in counting efficiency again is an exponential function.

Fig. 2 shows a typical quenching curve for tritium; increasing amounts of Hyamine solution are added to a tritium-labelled toluene standard.

This difference is probably caused by the very low energy of the beta-particles from tritium, so that very little quenching material is necessary to degrade some of the pulses and they are no longer detected at the photocathode.

The method of extrapolation to zero quenching by use of quenching curves has been suggested by C. T. PENG [6] for the routine measurement of tritium. The routine measurement of tritium in tissue samples, however, generally involves the counting of tissue from several animals; a quenching curve would therefore necessarily include tissue samples from different animals.

Experiments were performed in order to establish quenching curves for different tissue. Different amounts of tissue from several animals injected with tritium-labelled thymidine were counted, a standard amount of tritium-labelled toluene

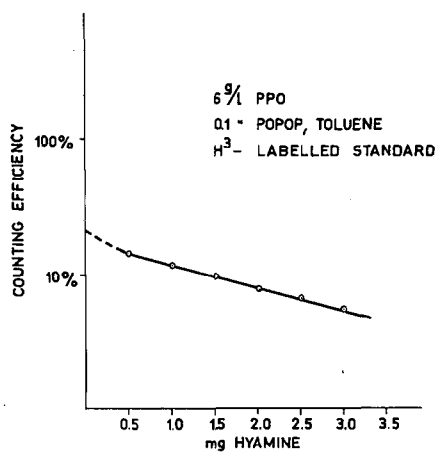


Fig. 2

Quenching effect of Hyamine upon the counting efficiency.

was added, the samples were recounted and the quenching was calculated for each sample.

Fig. 3 shows the quenching curves obtained for samples of intestine, testis and

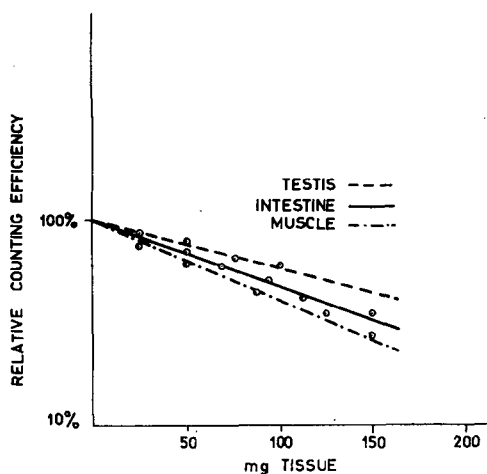


Fig. 3

Quenching effect of various tissues upon the counting efficiency.

muscle. For these organs exponential quenching curves were obtained, and the reproducibility was relatively good. With other organs such as thymus and spleen it was not possible to get reproducible results when organs from different animals

were examined. This is probably due to differences in the blood content of these organs, which again give different colour-intensities of the samples.

The extrapolation method therefore has its limitations in the application to routine counting of tissue samples.

These experiments, however, give valuable information as to the quenching properties of tissue samples.

### 3. Relationship between colour intensity and quenching

A method relating changes in counting efficiency to the colour intensity of the sample has been indicated by HERBERG [7]. He has reported that the reciprocal absorbance at 400 m $\mu$  of coloured solutions is a linear function of their counting efficiencies, and has shown this relationship for blood-digest solutions and different colouring agents.

Experiments were therefore performed to study the relationship between counting efficiency and colour intensity for tissue samples from various organs and over a wide range of concentrations. Samples were prepared as previously described and counted; a standard amount of tritium-labelled toluene was added, and the samples were recounted. The absorbance or extinction coefficient of the sample solution was measured in an Elko II colorimeter.

The colorimeter used is a filter photometer; the extinction coefficient was measured at the intervals 420, 450, 470, 530 and 590 m $\mu$ .

All the tissue samples investigated showed a maximum absorbance at 420 m $\mu$ . Since the secondary phosphor POPOP has a maximum in the emission spectra at approximately 420 m $\mu$  and the photocathode has its peak sensitivity at

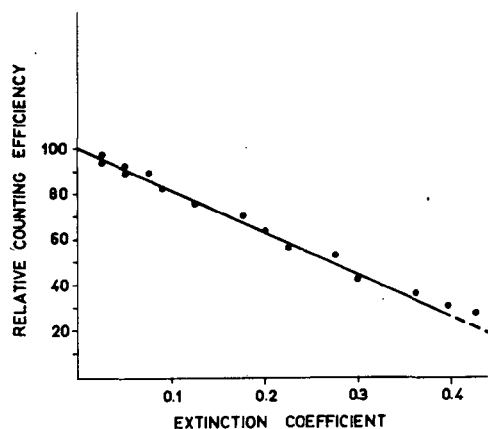


Fig. 4

Variation of counting efficiency with colour intensity.

420 m $\mu$ , it is evident that the strong absorbance of the solution at this wavelength will greatly influence the counting efficiency.

When the measured extinction coefficient of the sample solution was plotted vs. relative counting efficiency, a linear relationship resulted. The data from the measurements are shown in Fig. 4, and more details are given in Table I.

TABLE I  
VARIATION OF RELATIVE COUNTING EFFICIENCY WITH COLOUR INTENSITY

Tissue	Extinction coefficient	Relative counting efficiency
(Clear solution)		100
Liver	0.155	72
Liver	0.218	60
Liver	0.325	40.5
Spleen	0.338	38
Spleen	0.175	68
Intestine	0.085	83
Intestine	0.250	53.5
Skin	0.125	76.5
Testis	0.076	86
Kidney	0.300	42.5
Kidney	0.195	65
Muscle	0.095	79
Muscle	0.200	63

The extinction coefficient v. relative counting efficiency plot appears linear over a wide range of colour intensities. These data include colour measurements and counting efficiencies from various tissues, such as liver, spleen, intestine, skin, testis, kidney and muscles.

The established quenching curve was used for testing a series of unknown samples. The samples were run in duplicate, and the relative counting efficiency was determined both by means of the quenching curve and by the internal standard technique. The results, shown in Table II, indicate that the colour-

TABLE II  
QUENCHING CORRECTION BY INTERNAL STANDARD TECHNIQUE AND BY QUENCHING CURVE

Sample	Internal Standard		Quenching curve	
	Relative counting efficiency	Corrected cps	Relative counting efficiency	Corrected cps
120	$80.5 \pm 2.5$	$150 \pm 5$	$80.0 \pm 1.0$	$148 \pm 2$
260	$61.0 \pm 3.0$	$426 \pm 22$	$62.0 \pm 1.5$	$420 \pm 10$
285	$52.0 \pm 2.0$	$549 \pm 21$	$51.5 \pm 1.0$	$555 \pm 10$
25	$70.5 \pm 2.5$	$35.5 \pm 1.3$	$71.0 \pm 1.0$	$35.2 \pm 0.4$
120	$65.0 \pm 3.0$	$186 \pm 10$	$64.5 \pm 1.5$	$186 \pm 4$
480	$69.0 \pm 3.5$	$697 \pm 35$	$68.5 \pm 2.0$	$700 \pm 20$
930	$72.0 \pm 2.5$	$1295 \pm 45$	$70.0 \pm 2.0$	$1330 \pm 40$

measurement method is more accurate and dependable than is the internal-standard technique alone.

The former method makes use of many observations at varying sample concentrations, while the internal standard technique alone is encumbered with the statistical errors from counting and recounting of a single sample.

Applied to routine counting of a great number of samples, the method has the advantage that, once the quenching curve is determined, only one counting operation is necessary for each sample.

## PHOSPHORESCENCE

When the counting vial is exposed to light, it may become photoactivated, which will give rise to a high counting rate if it is counted immediately in the liquid scintillation counter. If the sample is kept in the darkened refrigerator for approximately one hour before being counted, the counting rate will return to normal background level. Vials containing Hyamine and scintillation solution give spuriously-high counting rate before being cooled. This phenomenon has been reported by VAUGHAN *et al.* [8] and is thought to be a thermal-activated chemiluminescence effect. However, a two-hour cooling time of the sample before counting is sufficient to yield a normal background level.

Another source of spurious counts seems to be of more importance for the counting of tritium in tissue samples. HERBERG [9] has reported that non-radioactive proteins in Hyamine solution may cause a high counting rate. The same effect was observed during this work and was found to be most marked in samples of blood and blood-containing tissues. This is most likely a chemiluminescence effect since, once the non-active samples are brought back to a normal background level, the same effect is not restored even if samples are kept in the daylight for days. This chemiluminescence has two components, one with a half-life of 3–4 min and another with a half-life of 6–7 h.

The first component has the higher counting rate, in the order of ten thousand cpm, while the second component has a counting rate of only a few hundred cpm.

The second component, however, can be a serious source of error, especially for the counting of samples of low activity. HERBERG [1] has also reported that acidification of the sample before counting will eliminate this phosphorescence.

Unfortunately, this acidification also may cause phase separation in the sample, especially when the wet tissue is dissolved directly. When the samples are cooled to  $-20^{\circ}\text{C}$  this is almost always the case. It was therefore found impracticable to use acidification of the sample before counting.

## SUSPENSION COUNTING

If the sample cannot be dissolved in the scintillator or in any mixture of solvents, it may be possible to count the sample in a suspension. Suspension counting was first reported by HAYES [10] and by WHITE [11].

The suspension-counting technique has been used successfully for the counting of carbon-14 and other low-energy beta emitters. Tritium, however, emits beta particles of a far shorter range (maximum range, about  $6\mu$  in a medium of unit density), and the problem of self-absorption therefore becomes the main difficulty in the suspension counting of tritium.

Bone samples are insoluble in the Hyamine; the possibility of counting these samples in a suspension was therefore investigated. The dried samples were ground to a fine powder and passed through a standard sieve (200 mesh) for selection of particles of constant size in an attempt to obtain a constant self-absorption factor.

A finely divided silicon dioxide (Aerosil) was used as the suspending agent; Aerosil combined with toluene gives a gel which possesses excellent supporting strength for solid particles. Samples are prepared for counting by addition of the gel to the glass bottles containing the pre-weighed samples. Samples prepared this way are stable for weeks without showing any settling of the fine particles.

Bone samples labelled with tritiated thymidine were counted in suspension with an efficiency of 6%.

Concentrations from 1—20 mg per 20 ml of gel showed no quenching effect, and the results were reproducible.

#### SENSITIVITY OF THE COUNTING METHOD

The real limitation in the sensitivity for liquid scintillation counting is the large number of background pulses arising in the counter itself.

For work with a single phototube liquid scintillation counter, the only possible way to reduce this background is to operate the counter at a low temperature. During this work the counter was kept at a temperature of  $-20^{\circ}\text{C}$ ; in this way it was possible to reduce the background to  $12 \pm 2$  cps. When the counter was continuously operated during a working day, the background increased to  $15 \pm 3$  cps. For low-activity measurement it was therefore necessary to include frequent counting of the background. For coloured solutions the background is also quenched to some degree, this has to be compensated for in the measurement of low-activity samples.

If a counting rate of approximately half of the background, on the average 6 cps, is considered as the detection limit, the limit of sensitivity for unquenched samples will be  $10^{-3} \mu\text{C}$  tritium per sample. Due to quenching effect in the tissue sample, it will be a sample weight giving optimum counting rate for that particular sample.

When the counting efficiency decreases as an exponential function of sample concentration, as previously shown, the following relationship has been established by PENG [5, 6]:

$$C = C_0 \cdot x e^{-\mu x} \quad (1)$$

where  $C_0$  is the specific counting rate of the compound (zero quenching),  $\mu$  is the quenching constant and  $x$  is the sample concentration. This equation has a maximum value for  $C$  when  $x = 1/\mu$ , then:

$$C_{\text{max}} = \frac{C_0}{e\mu} \quad (2)$$

Table III shows the sample concentrations and gives optimum counting rate

TABLE III  
OPTIMUM SAMPLE WEIGHT, COUNTING EFFICIENCY AND LIMIT OF  
SENSITIVITY FOR TRITIUM COUNTING IN TISSUES

Tissue	Optimum weight (mg wet tissue)	Counting efficiency (%)	Limit of sensitivity ( $\mu\text{C}/\text{mg}$ )
Testis	195	5.2	$1.6 \cdot 10^{-5}$
Intestine	145	4.9	$2.8 \cdot 10^{-5}$
Muscle	110	5.0	$3.0 \cdot 10^{-5}$
Liver	100	4.5	$3.5 \cdot 10^{-5}$
Spleen	100	4.5	$3.5 \cdot 10^{-5}$
Blood	25	4.3	$1.5 \cdot 10^{-5}$

for some of the tissues investigated. It also shows the corrected counting efficiencies at these sample concentrations, together with the calculated sensitivity of the counting method for these tissues.



## Conclusion

The liquid scintillation counting of whole animal tissue is particularly useful for the assay of a large number of samples. The sensitivity achieved with a single phototube liquid scintillation counter seems to be sufficient for many applications. This method has been used in the study of the metabolic fate of tritium-labelled thymidine incorporated into DNA of various tissues in mice. A dose of approximately 1  $\mu$ c tritium per gram body weight was injected, and the activity could be followed for a period of one month.

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## DISCUSSION XX

**R. Lloyd** (United Kingdom): I would like to point out that if the speaker wishes to use the  $0 \times 7$  optical filter for reducing chemiluminescence from her samples, she will have to change the composition of her scintillator. This filter is designed specifically for use with p-terphenyl in toluene and its use with PPO and POPOP would so seriously reduce the counting efficiency that the system would be almost unusable.

**B. Gordon** (United States of America): Besides absorbing light, there are other ways in which solutes will quench. Certain clear solvents, such as alcohols or aldehydes, may actually interfere with the energy transfer between the scintillating solvents and the phosphor. The use of the extinction coefficient to correct for quenching is applicable only when the photons emitted by the phosphors are absorbed. When the quencher interferes with the energy transfer between the solvent and the phosphor, the solution may of course be entirely clear but strongly quenched. One must therefore be careful to determine by which mechanism the quencher acts before choosing the method to correct for quenching.

**K. Halvorsen** (Norway): Yes, I am fully aware of that. My only purpose was to show the specific applications for the counting of the tissue sample in those cases where the colour intensity of the sample really appears to be causing most of the quenching.



# A LOW-LEVEL GEIGER-COUNTER FOR TRITIUM

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Abstract — Résumé — Аннотация — Resumen

**A low-level Geiger-counter for tritium.** A cylindrical counter tube of volume 11 l was constructed which contains a number of anticoincidence wires surrounding a 2.9 l effective-volume centre-counter. The centre counter is separated from the anticoincidence section by a thin aluminized Hostaphan foil. Details of the construction are given. The counter filling gas consists of 30 mm ethylene, 40 mm argon and up to 700 mm sample hydrogen. An external quenching circuit with a 7 msec dead time effectively eliminates after-pulses. In a 30 cm iron shield, the counting rates of the centre counter with dead hydrogen gas are 350 counts/min without and about 3 counts/min with the anticoincidence circuit in operation. If it is assumed that 1 count/min above background is significant, a T/H ratio of as low as  $10^{-16}$  can be measured without isotope enrichment. Experiments are in progress to check the longtime stability of the arrangement.

**Compteur Geiger à faible mouvement propre pour le tritium.** Les auteurs ont monté un tube compteur cylindrique d'un volume de 11 litres qui contient un certain nombre de conducteurs d'anticoincidence entourant un compteur central d'un volume réel de 2,9 litres. Ce compteur central est séparé de la zone d'anticoincidence par une feuille mince d'«Hostaphan» recouverte d'aluminium. Les auteurs donnent des détails sur le montage de l'appareil. Le mélange gazeux remplissant le compteur se compose d'éthylène (30 mm), d'argon (40 mm) et de l'échantillon d'hydrogène (jusqu'à 700 mm). Un circuit coupeur externe ayant un temps mort de 7 ms élimine efficacement les impulsions retardées. Avec une protection de fer de 30 cm, les taux de comptage du compteur central, rempli d'hydrogène inerte, sont de 350 coups par minute et d'environ 3 coups par minute, selon que le circuit d'anticoincidence fonctionne ou non. Si l'on suppose qu'un coup par minute au-dessus du bruit de fond est significatif, on peut mesurer des rapports T/H jusqu'à  $10^{-16}$  sans avoir à procéder à un enrichissement. On effectue actuellement des expériences pour contrôler la stabilité à long terme du système.

**Счетчик гейгера с низким уровнем для трития.** Была сконструирована цилиндрическая трубка с объемом в 11 литров, которая содержит ряд проводов антисовпадения, охватывающих центральную часть счетчика емкостью в 2,9 литра. Центральная часть счетчика отделена от секции антисовпадения тонкой алюминированной Гостафановой фольгой. Приводятся подробные данные конструкции. Газ для наполнения счетчика состоит из 30 торр этилена, 40 торр аргона и до 700 торр образца водорода. Внешняя цепь гашения с мертвым временем в 7 мсек. успешно устраняет последующие импульсы. В 30 см железном экране скорость отчета центральной части счетчика с «мертвым» водородным газом составляет 350 отсчетов в минуту без цепи антисовпадения и около 3 отсчетов в минуту с цепью антисовпадения. Если предположить, что 1 отсчет в минуту выше фона является значительным, то даже такое низкое соотношение T/H как  $10^{-16}$  можно измерить без обогащения изотопов. Ведутся эксперименты по проверке работы устройства на продолжительность времени.

**Contador Geiger de baja actividad de fondo para tritio.** Los autores construyeron un tubo contador cilíndrico de 11 l que contiene una serie de conductores de anticoincidencia en torno a un contador central de 2,9 l de volumen efectivo. La sección de anticoincidencia está separada del contador central por una delgada hoja de Hostaphan aluminizada. En el trabajo figura una serie de detalles constructivos. El gas que llena el contador consiste en una mezcla de etileno a 30 mm, de argón a 40 mm y la muestra de hidrógeno hasta 700 mm. Un circuito de extinción externo, cuyo

tiempo muerto es de 7 ms, elimina eficazmente todos los impulsos demorados. Con un blindaje de hierro de 30 cm, el índice de recuento del contador central con hidrógeno gaseoso inerte es de 350 impulsos/min cuando el circuito de anticoincidencia no funciona y de unos 3 impulsos/min en el caso contrario. Suponiendo que un valor de 1 impulso/min por encima de la actividad de fondo sea significativo, resulta posible medir razones T/H muy pequeñas, hasta  $10^{-16}$ , sin necesidad de proceder a un enriquecimiento isotópico. Se siguen realizando experimentos para verificar la estabilidad a largo plazo del dispositivo.

## Introduction

Three methods have been used successfully to detect tritium in low-level quantities: gas counting in the Geiger region, gas counting in the proportional region, and liquid scintillation counting. Of these, the gas counting methods have the advantage of high detection efficiency but the disadvantage of restriction to small sample sizes. Thus, enrichment procedures have been employed to bring the counting rate above the detection limit resulting from the background counting rate and its uncertainties. However, in the enrichment process a new uncertainty is encountered resulting from the poorly-known enrichment factor.

In order to reduce the necessity of enriching the sample or to avoid it altogether, a large counter of low background is required which will operate at reasonably high hydrogen gas pressures. For reliability reasons it is felt desirable that the counter should operate in the Geiger region.

## Construction of the counter

The construction is similar to the one proposed by HOUTERMANS *et al.* [1] (see Fig. 1). The total volume of the counter is about 11 l. The outside mantle consists of a brass cylinder closed on one end and flanged on the other where the front cover (1) is attached and tightened by means of a rubber ring and 12 screws. A somewhat smaller second brass cylinder (2) is cut into three pieces parallel to the axis, and the three pieces screwed separately to the front cover. Inside the second cylinder the supporting rings for the anticoincidence wires (3) and the foil (4) are mounted. In this way, all parts of the counter are accessible and the foil as well as the anticoincidence wires can easily be assembled. Insulation of the wires is achieved by "Teflon" spacers (5) between the supporting rings and their mounts. The anticoincidence wires are kept under tension by a spring arrangement (6) by means of which one of the supporting rings can be adjusted. In a similar way the foil can be strained until all wrinkles have disappeared. Finally, the centre wire (7) is inserted and kept under tension by a Y-shaped spring (8) at the back end of the counter. A "Teflon" pearl (9) insulates it from the wire. On both ends, the centre wire is led through a piece of copper capillary tubing (10) of about 40 mm length to ascertain proper anticoincidence shielding at the ends of the active volume. The wires are of 50  $\mu$  stainless steel. All dust particles have to be removed carefully before operation of the counter. The anticoincidence wires are all connected in parallel. Separate cables for the anticoincidence and the centre wire voltage are led through the front cover plate by means of ceramic insulators. The mantle is connected to ground potential.

The active "sample" volume between the ends of the capillary tubes and the foil is 2.9 l. The counter is evacuated and filled with the same gas mixture both in the anticoincidence and the centre volume. The filling consists of 30 mm ethylene, 40 mm argon, and up to 700 mm H<sub>2</sub>.

### Electronic circuit

The electronic circuit consists of two separate quenching units which are triggered by pulses of 5 V and generate a pulse which lowers the wire potential by 150 V, i.e. below the Geiger threshold, for an adjustable time interval in the

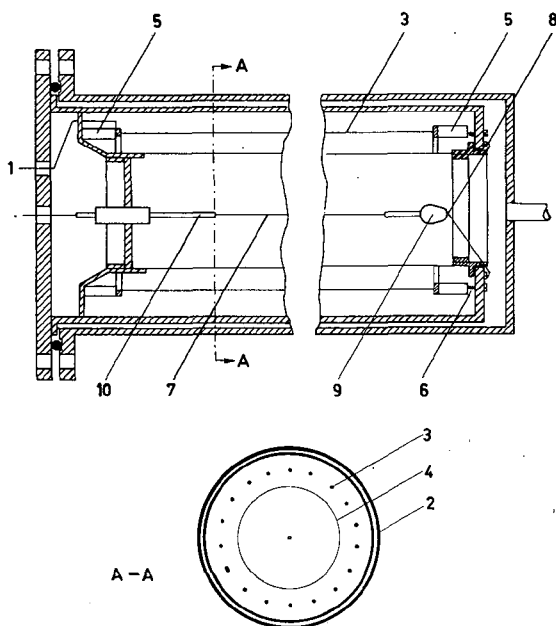


Fig. 1

Schematic diagram showing the counter construction. (1) Front cover plate; (2) second inside cylinder; (3) anti-coincidence wires; (4) foil; (5) "Teflon" spacers; (6) spring arrangement to keep the anti-coincidence wires under tension; (7) centre wire; (8) Y-shaped spring to keep the centre wire under tension; (9) "Teflon" insulation pearls; (10) copper capillary tubes.

millisecond range. In this way, after-pulses are avoided. An anticoincidence unit allows such centre wire counts only to be recorded which do not occur simultaneously with a count of the anti-coincidence wires. To achieve exact operation, the centre counts are delayed by  $3 \mu\text{sec}$  before entering the anticoincidence unit. The counts in both channels and the anticoincidences are fed into scalers and recorded; in addition the scaled-down pulses produce marks on a moving chart recorder to test the reliability of the measurement.

### Performance of the counter

Plateau curves were obtained (a) keeping the voltage of the centre wire constant and varying the voltage of the anti-coincidence wires (see Fig. 3), and (b) keeping the voltage of the anti-coincidence wires constant and varying the centre-wire voltage (see Fig. 2). The plateaux are fair and show the insensitivity of the device against high voltage drifts.

The counter is placed inside a 30 cm iron shield for the low-level measurements. Fig. 4 shows a background test run which was taken with a filling of 30 mm

ethylene, 40 mm argon, and 550 mm inactive tank hydrogen gas, the counter foil being of  $8.9 \text{ mg/cm}^2$  Cu. The errors indicated are the statistical errors for one hour of counting. The mean deviation of the single measurements results from statistical fluctuations only. The average background counting rate is seen to be close to 4 counts/min. The variations of this counting rate from one filling to the other

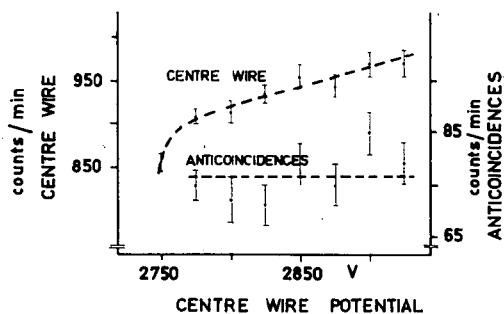


Fig. 2

Plateau curves taken at a constant anticoincidence-wire potential of 2460 V. Filling mixture: 30 mm ethylene, 40 mm argon, 550 mm hydrogen gas. Foil:  $10 \mu$  Cu. Length of quench pulses: centre-wire circuit 11.0 ms, anticoincidence-wire circuit 7.8 ms. Measurement outside iron shield.

and from day to day are less than  $\pm 0.2$  counts/min. It is hoped to reduce this figure in the future.

The background counting rate depends markedly on the hydrogen gas partial pressure as is seen on Fig. 5. This is probably due to interaction of  $\gamma$ -rays and neutrons with the hydrogen gas. Experiments to eliminate the neutron flux at the position of the counter are planned.

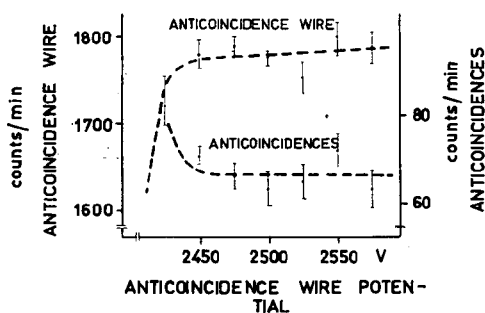


Fig. 3

Plateau curves taken at a constant centre-wire potential of 2800 V. Filling mixture, foil, and quench pulses as in Fig. 2.

Tests with different foils have resulted in an increase of counting rate with foil thickness of roughly 1 count/min  $8.9 \text{ mg cm}^{-2}$  for Cu-foils. The ideal foil, however, is one which has a thickness only slightly larger than the range equivalent of the most energetic tritium  $\beta$ -rays. A double-aluminized Hostaphan (Mylar) foil of  $20 \mu$  thickness has proved to fulfil this requirement, and a background counting rate with 550 mm partial pressure of hydrogen gas as low as 2.4 counts/min can be obtained.

To evaluate the usefulness of such a counter and compare it with other equipment, a figure of merit must be chosen which will contain the necessary information. One possibility is to use the number of T.U.s in the sample which can be measured in a given time interval  $t_s$  to within a given statistical error  $p$ . This number,  $F$ , depends

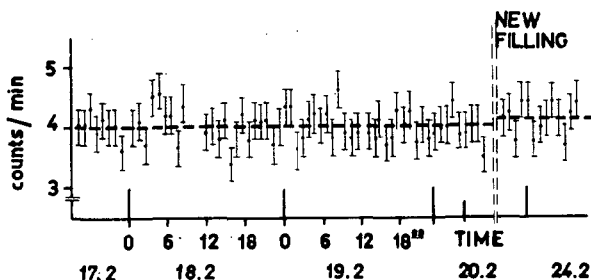


Fig. 4

Background test run. The anticoincidences are shown as a function of time for two different fillings of the counter. Filling mixture: 30 mm ethylene, 40 mm argon, 550 mm inactive tank hydrogen gas.

on the background counting rate, its uncertainty, and the efficiency of the detection device through the relation

$$F = \frac{s}{0.129 \eta n} (\text{T.U.}). \quad (1)$$

Here,

$$s = \frac{1}{2p^2 t_s} + \left( \frac{1}{4p^4 t_s^2} + \frac{b}{p^2 t_s} + \left( \frac{\Delta b}{p} \right)^2 \right)^{1/2} \quad (2)$$

is the corresponding sample counting rate in counts/min,  $b$  the background counting rate in counts/min,  $\Delta b$  its uncertainty in counts/min,  $\eta$  the efficiency of the detector, and  $n$  the number of moles of  $\text{H}_2$  from which the radiation is counted. The numerical

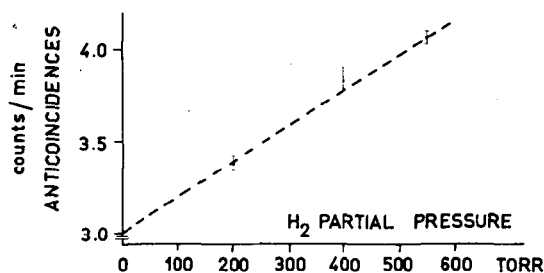


Fig. 5

Variation of background counting rate with partial pressure of inactive tank hydrogen gas.

factor 0.129 represents the number of disintegrations/min in 1 mole of hydrogen gas with a concentration of 1 T.U.

Table I lists the  $F$  values obtained by different authors with different detectors. In evaluating the data,  $t_s$  was arbitrarily chosen to be 5 h and  $p$  to be 5%. It is seen that the counter described in the present article compares favourably with the other detection devices.

TABLE I  
COMPARISON OF THE FACTORS OF MERIT  $F$  OBTAINED BY DIFFERENT  
AUTHORS

Method	$n$ (mole)	$b$ (counts/ min)	$\Delta b$ (counts/ min)	$\eta$ (%)	$s$ (counts/ min)	$F$ (T.U.)	Author	Ref.
Liquid Scintill. Proport.	1.75	100.5	0	6.34	12.3	860	HOURS and KAUFMAN	[2]
Counting	0.0041	0.58		$\approx 100$	1.75	3300	GEISS <i>et al.</i>	[3]
Counting	0.0166	5		90	3.0	1550	GONSIOR	[4]
Geiger	0.0097	8		$\approx 100$	4.0	3200	KAUFMAN and LIBBY	[5]
Counting	0.0023	1.50		$\approx 100$	2.25	7600	BROWN and GRUMMITT	[6]
Counting	0.040	2.25	0	94	2.5	530	ÖSTLUND	[7]
Counting	0.088	2.4	0.2 (0)	$\approx 100$	5.12 (2.60)	450 (230)	(this paper)	

Of course, the requirement that  $t_s$  be 5 h and  $p$  be 5% can be loosened. If it is assumed that 1 count/min above background is significant, it is possible to measure with the counter tritium concentrations of about 80 T.U. without enriching the tritium in the sample.

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## DISCUSSION XXI

**D. B. Smith** (United Kingdom): I should like to ask whether this is the most suitable method of detecting tritium in an enriched sample. Dr. Von Buttlar utilizes a volume of 2.9 l of gas but has to prepare 11 l, thereby reconcentrating over three times as much water as he uses. Would not a slightly higher background counter, utilizing all the gas prepared, provide a more efficient method of counting?

**H. Von Buttlar** (Federal Republic of Germany): I find that electrolysis procedures involving an order of a few milliliters are much more difficult than the conversion of about 10 ml into hydrogen gas. I therefore believe that our method is better, especially in the case of samples in which the level is not too low and which need not be enriched by more than about a factor of 10. It is easier to take a water sample from 100 ml down to 10.

**A. Nir** (Israel): The dependence of background on hydrogen pressure in Dr. Von



Buttlar's counter seems to be that which is characteristic for neutron scattering and capture. Has he tried to calculate the effect for this volume?

**H. Von Buttlar:** I have not done this yet because I do not know the neutron flux in my laboratory. I am trying to see what can be accomplished by inserting boric acid paraffin into the shielding. I have no idea as to the neutron effect on my counting rate.

**W. F. Libby** (United States of America): I would like to ask Dr. Von Buttlar, Prof. Östlund and Mr. Bainbridge whether the efficiency of the counters they have described has been tested by the use of standard tritium samples to see whether the counters are 100% efficient, except for end and wall losses. It has been my experience that the plateau slope can be good and yet the counter has inefficiencies.

**H. Von Buttlar:** We have tested our counter with a standard that is good only within 5% but within this error we have found no deviation. We are awaiting a standard from the National Bureau of Standards which we shall use to repeat the measurement.

**H. G. Östlund** (Sweden): We have used the original solution which we bought from the National Bureau of Standards as well as one obtained from the New England Nuclear Corporation. On the basis of our measurements, the latter solution appears to have been standardized within 0.5% of that of the National Bureau of Standards. Considering only the cylindrical volume around the central wire, the efficiency of our counter is 94.2%, at least I think that is what it was at the beginning. Allowing for reasonable end and wall effects, we arrive at something like 98% efficiency. This value has remained constant for a little more than 2 years.

**A. Bainbridge** (New Zealand): Just before this Symposium, I had a letter from Mr. B. J. O'Brien who was concerned over the fact that the sensitivity of his mixture was only 61% of the physical volume of the counter. It has not yet been determined whether a dilution error is involved, although it seems too large for that, or whether the counter is really inefficient. The La Jolla counter has been checked against Prof. Libby's standard and found to be within the expected range. We also have used a carbon-14 ethane standard in our counter and the agreement is satisfactory. O'Brien's problem still remains to be solved but, as far as I know, it did not arise in the case of the original ethylene argon mixture that I was using while I was in New Zealand.



# A HYDROGEN GAS COUNTING SYSTEM FOR NATURAL TRITIUM MEASUREMENTS

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Abstract — Résumé — АННОТАЦИЯ — Resumen

**A hydrogen gas counting system for natural tritium measurements.** An apparatus in which a water sample of about 1 g is reduced by magnesium to hydrogen and then fed directly to a 1-liter counting tube is described. The counting gas should contain 10 mm of propane in addition to 750 mm of the sample hydrogen. In conjunction with electronic quenching, this counter works in the Geiger region with excellent plateaux, reproducibility and long-range stability. With a heavy shielding and anticoincidence technique, the background is 2.25 cpm. Many present-day rains having tritium molar fractions of T/H of the order of  $6 \times 10^{-16}$  or more might be measured without enrichment, and in other cases the enrichment requirement is modest.

**Ensemble de comptage à hydrogène gazeux pour doser le tritium naturel.** L'auteur décrit un appareil dans lequel l'hydrogène provenant de la réduction par le magnésium d'un échantillon d'eau d'un gramme environ est amené directement dans un tube compteur d'un litre. Le gaz de comptage doit contenir du propane à la pression de 10 mm de mercure ajouté à l'échantillon d'hydrogène (750 mm de mercure). Avec le coupage électronique, ce compteur fonctionne dans la région de Geiger avec d'excellentes caractéristiques de palier, de reproductibilité, et de stabilité sur une longue période. Lorsque l'appareil est muni d'une protection épaisse et d'un dispositif d'anticoincidence, le bruit de fond est de 2,25 coups par minute. Il est possible de faire sans enrichissement la détermination quantitative du tritium des eaux de pluie actuelles qui contiennent des fractions molaires T/H de tritium de l'ordre de  $6 \cdot 10^{-16}$  ou davantage; dans d'autres cas, l'enrichissement nécessaire est faible.

**Водородная газовая счетная система для измерений естественного трития.** Описывается прибор, в котором проба воды весом в 1 грамм превращается с помощью магния в водород, который непосредственно направляется в счетную трубку емкостью 1 литр. Газ в счетнике должен содержать 10 мм пропана в дополнение к 750 мм водородной пробы. Вместе с электронным гашением этот счетчик работает в зоне Гейгера с отличными плато, воспроизводимостью и долговременной постоянностью. При тяжелой экранировке и технике антисовпадений фон равен 2,25 отсчетов в минуту. На сегодняшний день многие дождевые осадки с молярными долями трития T/H порядка  $6 \times 10^{-16}$  или более могут быть измерены без обогащения, а в других случаях требуется незначительное обогащение.

**Dispositivo de recuento de hidrógeno gaseoso para el análisis de tritio natural.** El autor describe un aparato en el cual una muestra de agua del orden de 1 g se reduce, por acción del magnesio, a hidrógeno que se introduce directamente en un tubo contador de 1 l de capacidad. El gas de recuento debe contener propano a la presión de 10 mm de Hg, además de la muestra de hidrógeno a 750 mm de Hg. Con un sistema de extinción electrónica, este contador funciona en la región de Geiger con excelentes características de rellano, de reproductibilidad y de estabilidad a largo plazo. Al utilizar un blindaje grueso y un procedimiento de anticoincidencias, la actividad de fondo es de 2,25 impulsos por minuto. El tritio de muchas aguas pluviales, que presentan fracciones molares de T/H del orden de  $6 \times 10^{-16}$  o superiores, podría determinarse cuantitativamente sin enriquecimiento previo o con sólo un enriquecimiento moderado.

## 1. Introduction

The difficulties in making measurements of tritium in natural water are certainly part of the reason why so few laboratories have done this kind of work. Most water samples have to undergo enrichment in order to reach a measurable specific activity. Even then the obtained count rates from tritium are so low that background is a serious problem, which necessitates the same use of heavy shielding and anticoincidence techniques as is required in radiocarbon dating work. This paper will deal exclusively with the counting equipment used at our laboratory, our enrichment system being described in a separate paper [1].

Our work was first concentrated on making a counting system which could handle a large quantity of water and give high efficiency with a low and reliable background count rate for work in the Geiger region, since the primary ionizations caused by tritium are very weak. Moreover, it should be ready for use immediately after being filled and should be furnished with a chemical system, starting with water yielding close to 100%, without isotopic fractionation, and free from memory effects. After several attempts with previously known counting methods and their variations, we finally arrived at the system described below. The choice seems to us to have most of the desirable qualifications.

## 2. Chemical apparatus

The chemistry involves the reduction of 1.1 ml of water to hydrogen by hot magnesium. This hydrogen is then fed directly to the counter without the use of any pumping devices.

A simplified scheme of the reduction and filling system is given in Fig. 1. Thirty

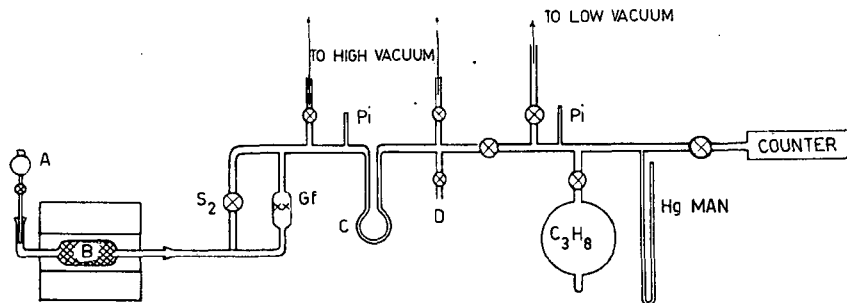


Fig. 1

Simplified diagram of the chemical system.

Pi: Pirani gauge tube.

Hg Man: Mercury manometer.

g of magnesium turnings (Grignard reagent) is charged in the wide part of the heat resisting glass reduction tube B and kept in place by two loose quartz wool plugs. The water sample is introduced into the small drop funnel A. During the warm-up time of the furnace, the counting tube and the reduction system are pumped alternately. The dust filter Gf is a fritted glass filter of the porosity grade 5 (pore diameter about  $1.2 \mu$ ). This filter acts as an obstacle to obtaining good vacuum and is therefore by-passed through stopcock S2 during pumping. When the automatically regulated furnace has reached its equilibrium value of  $590^\circ\text{C}$ , the water trap C is cooled by dry ice trichloroethylene, the pumping is stopped, and the stopcock S2

is closed. After a final pumping of the counter and checking that the vacuum is better than 0.001 mm Hg, 10 mm of propane is introduced. Water is now sucked into the protruding part of the reduction tube dropwise, where it evaporates and the vapour is reduced to hydrogen. This reaction is vigorous, and the water addition has to be made carefully so that the temperature does not exceed 600 °C by more than a few degrees. At higher temperatures the magnesium or its oxide reacts considerably with the glass, and, furthermore, the softening point of the glass is reached. At temperatures below about 570 °C the reaction tends to be incomplete, with the resulting danger of isotope fractionation.

When the hydrogen pressure exceeds 12 mm, the gas is led directly to the counting tube through the freezing trap. By gentle heating with a flame on the protruding part of the reduction tube the water is boiled off, drop by drop; and in about 30 minutes the pressure builds up easily to 760 mm Hg, after which the counter is sealed off. At this moment no water, or only very little, should be left inside the reduction tube, thus avoiding possible fractionation owing to the difference in vapour pressures of H<sub>2</sub>O and HTO. Normally no trace of water appears in the cold trap. The counter is ready for use immediately, no further mixing being necessary. The magnesium is used only once; thus there is no danger of cross-contamination of samples owing to memory effects here. The hot zone of each reduction tube will hold for a few runs, after which the chamber B is replaced.

Tank hydrogen for background counting and "spiked" hydrogen for standardization can be introduced at D. Otherwise a small ampoule can be attached here for sampling of the hydrogen for mass-spectrometric deuterium measurement.

The total gas-filled volume of the entire system is 1420 ml. Taking into account the different temperatures and partial pressures, this corresponds to 1.04 g of water. The water quantity introduced into the vacuum system is 1.07 g, determined by differential weighing. The chemical yield is thus 97% ( $\pm 2\%$ ), and no chemical fractionation is expected.

### 3. Counting tube and shielding

The counting tube, Fig. 2, is made from a copper tubing with an inner diameter of 51 mm and wall thickness of 1.5 mm. The end-walls (T) are made of polytetra-

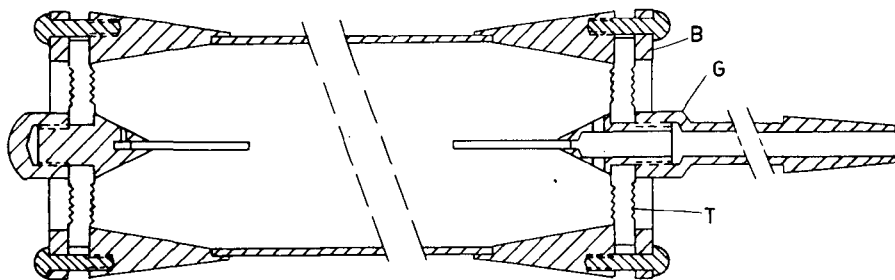


Fig. 2  
Construction of the counting tube.

fluoro-ethene, clamped to the tube by means of brass rings (B), fastened by screws. The anode is a 0.12 mm stainless steel wire (Sutur wire) with an unshielded length of 476 mm. The gas inlet and anode support (G) is made of brass. If the active counting volume is presumed to be a cylinder with the same length as the exposed

part of the centre wire, this volume is 972 ml, corresponding to 0.711 g of water in the form of hydrogen at 750 mm Hg and 25 °C.

The counter is surrounded, in turn, by 25 mm of pure lead [2], 18 cosmic ray G-M counters of 1 m length and 9800 kg of iron. A layer of 250 kg paraffin wax, containing 20 kg of boric acid, is sandwiched between the iron for the purpose of trapping neutrons.

#### 4. Electronic equipment

The tritium counter is used with an electronic quenching circuit, Fig. 3, which triggers at about 0.5 V negative pulse on the centre wire and provides a quenching pulse of 180 V (square wave), with a duration depending on the megohm resistor  $R_x$ .

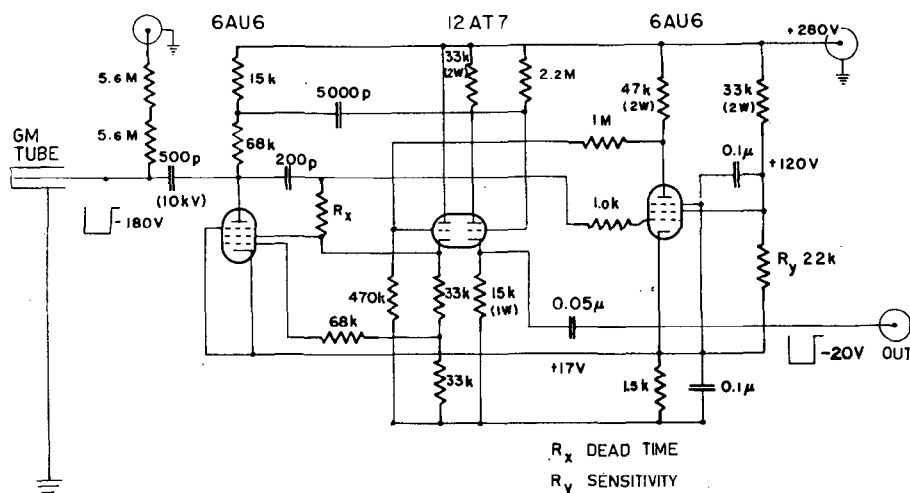


Fig. 3

Diagram of the quenching circuit.

in the figure. The pulse length chosen is 1000  $\mu$ s. The pulses are also fed to an anticoincidence unit, where they are differentiated and delayed 10  $\mu$ s. The ring of G-M counters is also quenched electronically for better stability and longer lifetime. The anticoincidence unit feeds three scalars, one for the ring counts, one for total counts in the tritium counter and one for the net counts, i. e., the tritium plus the residual background.

#### 5. Counting characteristics

Several attempts have been made to count in pure hydrogen, with and without external quenching, both at low gas amplification, in the proportional region, and at high gas amplification, in the G-M region; but these experiments were not successful. However, even very minute quantities of propane drastically improve the behaviour of the hydrogen counter. Such mixtures have been used for some years in tracer techniques by MELANDER [3] at total pressures below 100 mm Hg. We found that this combination of external quenching and a few mm of propane gave excellent performance at higher hydrogen pressures.

A quench time of 1000  $\mu$ s was chosen although any time longer than about 650  $\mu$ s was enough at 1 atm of hydrogen. The working voltage for Geiger counting at that pressure is about 3400 V for 5 to 15 mm of propane, giving a 150 V plateau with a slope of 2 to 3% per 100 volts. Both lower and higher propane pressures give higher threshold, and propane pressures below 2 mm give irregular performance.

With 10 mm of propane the plateaux were equally good at any hydrogen pressure from 250 to 800 mm Hg, the highest pressure tested.

## 6. Performance of the entire system

### (a) BACKGROUND

The residual background count rate after anticoincidence is 2.25 cpm. This has been measured repeatedly with seawater collected in 1947, between measurements of unknown samples. The barometer coefficient is less than 0.003 cpm/mb. These background count rates are normally reproducible within the statistical errors ( $\pm 0.05$  for 20 hours of counting) if the counter is pumped for at least  $1\frac{1}{2}$  hours after the preceding sample, which should not have exhibited more than a few hundred cpm. After a "hot" sample, e. g. 300 cpm or more, the same treatment sometimes results in an extra background of up to 0.1% of the count rate of the preceding sample. If the pumping time is increased to two one-hour periods with an interim flushing with inactive hydrogen, the memory effect disappears completely. Within a series of samples of low activity this problem is certainly not critical.

The average meson count rate (coincidences) is 144 cpm, subject to normal dependence of barometric pressure and cosmic conditions.

### (b) ABSOLUTE EFFICIENCY

The values of absolute disintegration rates in this work refer to a standard sample of tritium water delivered by the New England Nuclear Corp., Ltd., Boston, Mass., with the designation "Standard Source NES — 3", which was stated to contain tritium corresponding to  $1.96 \times 10^6 (\pm 3\%)$  d min<sup>-1</sup> ml<sup>-1</sup> as of 6 February 1959. According to our measurements, this water standard agrees to within less than  $\pm 0.5\%$  with the standard tritium water supplied by National Bureau of Standards, Washington, D. C., with  $1.33 \times 10^4 (\pm 1.5\%)$  d sec<sup>-1</sup> ml<sup>-1</sup> as of 20 August 1954. By dilution with inactive water, samples with known specific activity were prepared, reduced and measured under anticoincidence. The counting characteristics for tritium,

TABLE I  
COUNTING EFFICIENCY

Run No.	Dead time corrected count rate (cpm)	Equivalent water quant. (g)	Disintegration rate (d min <sup>-1</sup> ml <sup>-1</sup> )		Counting efficiency (%)
			measured	calc'd	
51	3653 $\pm$ 20	0.727*	5024	5341	94.1 $\pm$ 0.3
147	278.3 $\pm$ 2.0	0.711	391.4	417.7	93.7 $\pm$ 0.7
153	353.1 $\pm$ 2.4	0.711	496.5	530.0	93.7 $\pm$ 0.7
200	277.3 $\pm$ 1.5	0.711	390.0	412.5	94.5 $\pm$ 0.6
212	69.4 $\pm$ 0.8	0.711	97.6	102.9	94.9 $\pm$ 1.2
					Average 94.1

\* Wire length 490 mm.

checked at various tritium activities up to 3600 cpm, exhibited plateaux as good as, or better than, the  $\text{Co}^{60}$  plateaux. The working point was chosen 65 V above the starting voltage.

In the calculations necessary dead time corrections arising from the various blocking times of the anticoincidence and quenching circuits were taken into account. The results are reported in Table I. The efficiency figures were derived under the assumption of cylindrical geometry (see above, p. 336) with a counting volume corresponding to 0.711 g of water. For each value of efficiency the error given is based on counting statistics only, the 3% uncertainty of the standard itself not being included. The average of 94% efficiency is certainly reasonable, no corrections having been made for end effects and other disturbances. Calculated on the minimum required sample quantity of 1.1 ml of water, the overall efficiency is about 60%.

(c) REPRODUCIBILITY AND LONG TIME STABILITY

In order to prove the reproducibility of the whole reduction and counting system, *all* results on double checks made on tritiated water samples from 11 May to 15 July 1959 are recorded in Table II. Corrections have been made for background, filling

TABLE II  
DOUBLE CHECKS ON SAMPLES OF TRITIATED WATER

Water sample	Reduction (filling) No.	Net count rate (cpm)	Difference ( $D \pm \epsilon_D$ )	$D/\epsilon_D$
T 11	26	$64.4 \pm 0.9$	$-0.1 \pm 1.20$	$-0.08$
	75	$64.3 \pm 0.8$		
	28	$99.0 \pm 0.3$		
T 12	44	$99.6 \pm 0.7$	$+0.6 \pm 0.77$	$+0.78$
	79	$98.1 \pm 1.1$	$-1.5 \pm 1.26$	$-1.19$
	33	$62.4 \pm 0.5$	$-0.4 \pm 0.71$	$-0.56$
T 8	85	$62.0 \pm 0.5$		
	59	$57.9 \pm 0.6$		
T 11 E	86	$56.7 \pm 0.5$	$-1.2 \pm 0.79$	$-1.52$
	71	$176.2 \pm 1.7$	$+1.6 \pm 2.4$	$+0.67$
T 10 E	122	$177.8 \pm 1.7$		
	76	$96.7 \pm 1.2$	$-1.7 \pm 1.63$	$-1.04$
T 19	128	$95.0 \pm 1.0$		
	78	$97.2 \pm 1.2$	$-1.0 \pm 1.63$	$-0.61$
T 13	118	$96.2 \pm 1.0$		
	98	$265.5 \pm 2.6$	$+0.8 \pm 3.3$	$+0.24$
T 16 E	109	$266.3 \pm 2.1$		
	102	$157.5 \pm 1.1$	$+1.3 \pm 1.94$	$+0.67$
T 17 E	106	$158.8 \pm 1.6$		
	101	$(52.5 \pm 0.7)^*$	$-1.1 \pm 0.78$	$-1.41$
T 16	111	$46.8 \pm 0.6$		
	134	$45.7 \pm 0.5$		

\* The ratio coincidence counts/ring counts was incorrect, indicating that something was wrong with this filling.

pressure, temperature and radioactive decay between pairs of measurements, but not for dead time loss. The uncertainties given are the theoretical root mean square errors, derived from the numbers of collected counts only. A  $\chi^2$ -analysis of the values of  $(D/\epsilon_D)^2$  indicates that the experimental differences are those expected if



no other important source of error is present. From this result, together with the 97% chemical yield, it can be concluded that the reduction does not involve any measurable fractionation.

## 7. Conclusion

The features of the described counting system make it possible to determine T/H ratios in water down to  $500 \times 10^{-18}$  (500 T.U.), with a root mean square error of  $\pm 3\%$ , and at  $\pm 12$  T.U. at lower T/H-ratios, in about 1 ml of water, with counting periods of 1000 min. Since most rains are about 200 T.U. or lower and river water of the order of 10 T.U., most samples of natural water have to be enriched before counting. In comparison with that required in earlier work, however, the necessary degree of enrichment is appreciably smaller.

## ACKNOWLEDGEMENTS

This work was made possible by grants from Knut and Alice Wallenbergs Stiftelse and the Swedish National Science Foundation.

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- [2] BOLIDEN MINING CO., Sweden, Laisvall mine "Grade A" lead.
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## DISCUSSION XXII

**B. Grinberg (France):** Could Prof. Östlund give us some information on the origin of the low-level lead which he used in his installation, indicating the manner in which he selected it and also its activity by comparison with that of ordinary lead? Had he any special reasons for preferring magnesium to zinc for the decomposition of water and did he find that the decomposition by magnesium was fully reproducible? Was the device for low-level measurements installed in an ordinary laboratory or in an underground one? In certain cases, the latter location could give a considerable improvement in the background.

**H. G. Östlund (Sweden):** In reply to the first question, concerning our lead, I should mention first that we have been doing dating work with carbon-14 since 1954. We started by using triple distilled mercury in an iron tank but this is rather an expensive counting arrangement. When we were building our tritium counter, we succeeded in getting hold of some old lead from a church roof which had been laid in 1708. Although we had quite a lot of this lead at the start, unfortunately, most of it was later stolen. In our search for good, non-radioactive lead, we then turned to certain mining people in Sweden who made available two samples from the Laisvall mine in southern Lapland. These samples were designated Laisvall A and Laisvall B. We compared them with our church lead and with a piece of ordinary lead. With a thin wall counter, we got values of the order of 8 counts/min for the ordinary lead, 7 counts/min for the church lead, 7.5 counts/min for the Laisvall B lead and 6—6.5 counts/min for the Laisvall A lead. Thus, the Laisvall A type seemed to be slightly better than the old church lead which, in turn, was slightly better than ordinary lead. These measurements were very rough. We had to prepare the counter rather quickly and these were the only samples we

measured at that time. We have used this Laisvall lead for the tritium counter and for another carbon-14 counter which is being delivered from Stockholm to Miami, where I am at present setting up a carbon-14 laboratory station, and it is still giving the same good performance. We are going to buy a new lot of it in six months' time, for use in other carbon-14 counters, and I hope we will get the same quality again, but one can never be sure.

The second question is much easier to answer. There were two things which we did not like about zinc: first, we had some difficulty in, so to speak, starting the reaction with it (whether this was due to clumsiness on our part or to some other factor I do not know); and, secondly, once we got the reaction started, there was the problem of the zinc evaporating out into the vacuum system. We decided to try magnesium and it worked beautifully, just as we expected. We change the magnesium between every run, so that there is no danger of memory effects. The yield of this reaction has been tested several times — in so far as this is feasible — by weighing in water and by calculating on the basis of the volume and temperatures of the gas systems, and we always came very close to 100%, or at least to within 3% of this figure.

In reply to the third question: our laboratory is located on the ground floor of a large building. Above the laboratory there are additional floors of rather thin concrete. For some years, we also had the same apparatus on the ground floor of another building, with only one floor above the laboratory. The background for our carbon-14 counter was the same in both buildings. I would say this is a fairly normal location for a laboratory in which the floors have to bear a weight of about 10 t. I am quite sure that the background would improve considerably if we went down into the ground.

**B. Grinberg:** All the measurements we have been hearing about since yesterday, whether with liquid scintillators or with gas counters, pre-suppose previous standardization; this latter was always based on the National Bureau of Standards (NBS) standard which dates from 1954 and was measured calorimetrically. Even assuming this standard to be accurate to within 2—3% when it was made, the present values are vitiated by an additional error resulting from our lack of precise knowledge about the tritium half-life. As so many laboratories are doing tritium research, I wonder whether the National Bureau of Standards or some other laboratory should not prepare a new standard so as to eliminate this inevitable error connected with the half-life. If so, and it could be prepared during the coming year, and in view of the activities which appear to interest the participants here, the standard might have a weaker specific activity than the weakest 1954 standard which, as I recall, was  $1.33 \times 10^6$  disintegrations/sec/ml.

**W. F. Libby** (United States of America): I think it would be a good idea to have a new tritium standard calibrated and also to have it in a variety of dilutions. I believe that the National Bureau of Standards would be pleased to prepare them if this Symposium asked it to do so. I would suggest that we do ask, and then we could perhaps ask the Agency to help distribute them.

**D. Lal** (India): Could Prof. Östlund indicate the background counting rate of his system with and without the paraffin plus boric acid cover on the counter?

**H. G. Östlund:** I am afraid I cannot, but it seems to me that the paraffin-boric acid layer does have some effect on the background of the tritium counter. When we built the counter we did not intend to make an extensive study of all its parameters and of its anticoincidence behaviour, etc. On the other hand, two

substantial flares which occurred on 12 and 15 November 1960, respectively, resulted in a considerable increase in the cosmic neutron rate at certain hours. We have no findings for the first flare because the sample we had in the counter at the time contained too much activity for us to be able to observe anything unusual. In the case of the second flare, the overnight count (which was a background count) did not indicate any extra activity as far as the tritium counter was concerned but we did have an appreciable extra count rate in our carbon-14 counter at 3 atm  $\text{CO}_2$ . The latter counter is not well shielded from cosmic neutrons.

**F. Begemann** (Federal Republic of Germany): I have one additional comment on the question of the quality of the NBS standard. I think that there is no cause for concern with respect to the physical constants involved in these calculations, i. e., the half-life and the average energy of the tritium. The average energy of the tritium decay has been redetermined only recently and found to agree to within 0.5% of the figure used by the NBS in 1954 to calculate the activity. I believe that the figure for the half-life has not been changed by more than 0.5—1.0%. Of course, these remarks apply only to the physical constants which enter into the calculation — there might also have been mistakes in the 1954 measurements themselves.



# THE MEASUREMENT OF NATURAL TRITIUM LEVELS IN GEIGER COUNTERS

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Abstract — Résumé — Аннотация — Resumen

**The measurement of natural tritium levels in Geiger counters.** A method for the counting of tritium in a 300 ml gas counter with internal quenching gases is described. Originally a system with ethylene-argon as a quenching gas was used in conjunction with an anticoincidence ring. The anticoincidence count-rate plateau characteristics were unsatisfactory at low count rates because of unsatisfactory quenching, and a search was made for more efficient quenching gases. The source of the background count-rate plateau slope is discussed, and the properties required of a suitable quenching gas for hydrogen counting are given. Results of a study made of the counting characteristics of hydrogen quenched with benzene, ethyl-bromide, ethyl-ether, isopropyl amine, hexane, ethylamine and isoprene are given. Ethylamine and ether in particular gave very satisfactory quenching characteristics. A counting system with a counter filled with 40 cm of hydrogen and quenched with ethylamine is described. The background rate is 3 cpm with a comparatively flat background plateau.

**Détermination quantitative du tritium naturel par compteurs Geiger.** L'auteur décrit une méthode de dosage du tritium au moyen d'un compteur de 300 ml dans lequel on utilise des gaz de coupage internes. Il avait tout d'abord utilisé, comme gaz de coupage, un mélange d'éthylène et d'argon avec un anneau d'anticoincidence. Mais pour les taux de comptage faibles, les caractéristiques du palier, avec un montage en anticoincidence, n'étaient pas satisfaisantes en raison de l'insuffisance du coupage, et l'auteur a cherché un mélange plus efficace. Il analyse la cause de la pente du palier de la courbe du bruit de fond et énumère les propriétés que devrait présenter un gaz de coupage efficace pour le comptage de l'hydrogène. Il donne ensuite les résultats obtenus, au point de vue des caractéristiques du comptage de l'hydrogène, avec les substances de coupage suivantes: benzène, bromure d'éthyle, éther éthylique, isopropylamine, hexane, éthylamine et isoprène. Avec l'éthylamine et l'éther éthylique, les caractéristiques de coupage sont particulièrement satisfaisantes. L'auteur décrit un dispositif de comptage qui comprend un compteur rempli d'hydrogène à la pression de 40 cm de mercure, la substance de coupage utilisée étant l'éthylamine. Le bruit de fond est de 3 cpm, et la pente du palier correspondant relativement faible.

**Измерение уровней естественного трития в счетчиках Гейгера.** Дается описание метода подсчета трития в 300мл газовом счетчике с использованием газов для гашения. Первоначально была применена система с кольцом несовпадений при использовании этилен-аргона в качестве газа для гашения. Пологая часть характеристики скорости отсчета несовпадений была неудовлетворительной при низких скоростях счета, что объясняется плохим гашением, а поэтому были проведены поиски газов с более эффективным гашением. Рассматривается наклон пологой части характеристики скорости отсчета источника Фона, а также указываются необходимые свойства подходящего гасящего газа для отсчета водорода. Приводятся результаты изучения характеристик подсчета водорода, который гасится с помощью бензола, бромистого этила, простого этилового эфира, изопропилового амина, гексана, этил-амин и изопрена. В частности, этил-амин и эфир дают весьма удовлетворительные гасящие характеристики. Содержится описание счетной системы, использующей счетчик, наполненный до 40 см водородом и гасимый этил-амином. Коэффициент фона составляет 3 отсчета в минуту при сравнительно плоском фоне пологой части характеристики.

**Medición de concentraciones naturales de tritio mediante contadores Geiger.** El autor describe un método de análisis de tritio en un contador de 300 ml que funciona con arreglo al principio de la extinción interna por medio de gases. Originariamente se aplicó un sistema basado en el empleo de una mezcla de etileno y argón como gas extintor, en combinación con un anillo de anticoincidencias. Ahora bien, las características del rellano de la curva de recuento al emplear un circuito de anticoincidencias no resultaban satisfactorias cuando el número de impulsos era reducido, debido a una extinción deficiente, y por tal motivo se trató de encontrar una mezcla gaseosa más eficaz. El autor estudia la causa de la pendiente del rellano de la curva del recuento de fondo y enumera las propiedades que debe reunir un gas extintor adecuado para el recuento del hidrógeno. Detalla los resultados de un estudio de las características de recuento del hidrógeno usando como sustancias extintoras el benceno, el bromuro de etilo, el éter etílico, la isopropil amina, el hexano, la etilamina y el isopreno. Se comprobó que la etilamina y el éter etílico, en particular, presentan características de extinción muy satisfactorias. El autor describe un sistema de recuento basado en el empleo de un contador que se rellena con hidrógeno a la presión de 40 cm de Hg y en el cual se usa etilamina para la extinción. La actividad de fondo asciende a 3 impulsos por minuto, siendo relativamente débil la pendiente del rellano de la curva correspondiente.

## 1. Introduction

For some two years we have been making routine measurements of the tritium content of natural water samples collected in and about New Zealand. The samples, varying from 5 to 15 l in volume, are enriched in tritium by electrolytical reduction to a volume of about 0.5 ml in an electrolysis plant developed by A. E. Bainbridge. The samples are converted to hydrogen over zinc at 400°C. Since New Zealand is completely surrounded by oceanic waters, the natural tritium levels are relatively low. Also in the southern hemisphere thermonuclear weapon tests have caused a much smaller tritium fallout than have such tests in the northern hemisphere. Therefore, even after an enrichment of more than a thousand times, most samples contain activities of the order of 10 dpm or less.

In the counting equipment originally used at this laboratory, Geiger-Müller counters filled with hydrogen and quenched with a mixture of ethylene and argon, as used by KAUFMAN and LIBBY [1], were used. It was found that many samples, particularly those of geothermal origin, gave count rates lower than background.

An investigation into variations of the background counting rate was made, and it was found that some variation was caused by the large slope of the background count-rate plateau. This high-plateau slope was largely due to inefficient quenching.

This paper describes the results of an investigation to find quenching agents that would give more satisfactory quenching.

## 2. Counting equipment

The construction of counters No. 4 and 5, now used for counting the hydrogen samples, is shown in Fig. 1. The counter has a copper cathode (1) of diameter 1.5 in and thickness 1/16 in. The tungsten anode (2) is 0.004 in in diameter and is supported by the glass insulators (3).

The use of the polythene diaphragm valve (4), supplied by Metropolitan-Vickers Ltd., obviates the use of grease; and the kovar joint (5) connects the counter to a glass-ball socket, used on the vacuum system during filling. The preamplifier lead is attached to the electrical socket (6).

The prototype counters (No. 1 and 2) were basically similar to No. 4 and 5 except that they had removable ends, held on with black wax, and a glass tap.

The basic counting circuit is shown in Fig. 2. The counters are placed inside an anticoincidence ring, which itself is situated inside an 8 in thick iron shield. There are two complete circuits and normally two counters, filled with the same or

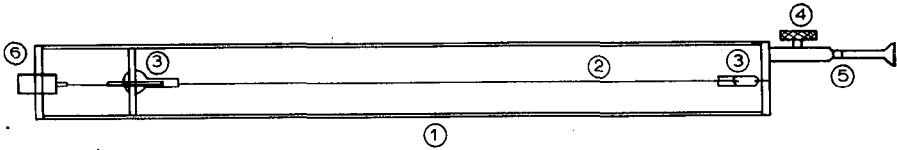


Fig. 1

Geiger counter No. 4.

different samples, are counted at the same time. The anticoincidence ring reduces the background rate from about 90 cpm to 2.7 cpm in the case of counters 4 and 5. The basic circuit is quite straightforward except perhaps for the correction voltage unit. This circuit, which was developed at this laboratory some years ago by G. J. Fergusson, enables a Geiger-Müller counter to be operated with a fixed-pulse-height output, independent of filling pressures, temperature and E.H.T. variations. The operation of the circuit is as follows:

If pulses greater in size than a certain discriminator setting enter the discriminator, they trigger a univibrator, the pulse from which charges a condenser in the

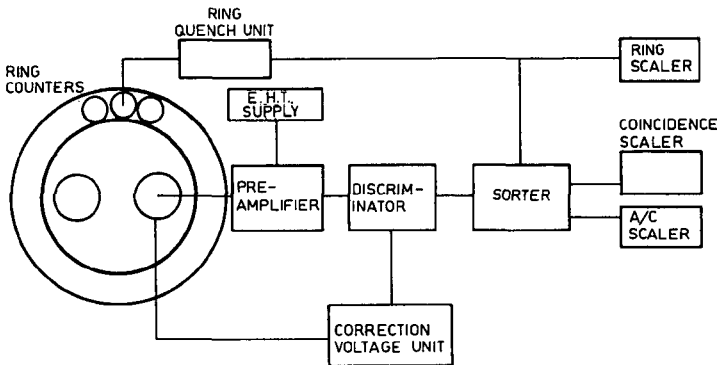


Fig. 2

Basic counting circuit.

grid circuit of a cathode follower. This charge raises the cathode potential; and, since this is connected to the cathode of the counter through a low-pass filter, the counter anode-cathode voltage drop is reduced. This in turn reduces the pulse height from the counters. The condenser circuit has a discharge time constant of about 10 min, so in practice the pulse height is kept at a steady level. The unit ensures the counter's operation at a fixed voltage above the knee of its plateau, irrespective of E.H.T. and pressure variations. Thus, it is unnecessary to make careful E.H.T. settings or to know the plateau characteristics when the counting tubes are filled at various pressures.

### 3. Gas quenching and background count rate

The anticoincidence background count rates for counters 1 and 2 are plotted in Fig. 3 — solid curves — against the discriminator pulse-height settings. The figures by the curves refer to the pressure of the "K" gas and hydrogen respectively in

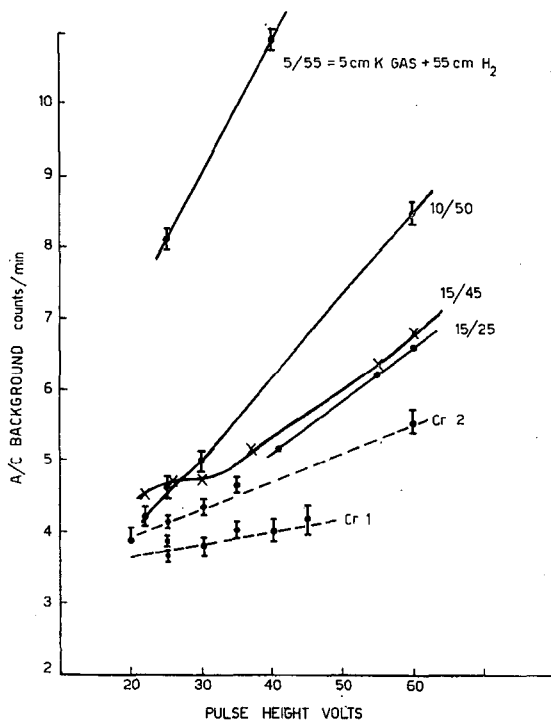


Fig. 3

Section of plateaux for counter.

cm of Hg. The "K" gas was composed of a mixture of four parts of ethylene and six parts of Argon. The E.H.T. changed with pulse-height setting by an amount roughly equal to double the change in pulse-height setting. Although an increase in the amount of "K" gas above 25% reduced the background slope slightly, there was no great improvement. When the pulses were inspected with the aid of an oscilloscope, it was found that large numbers of multiple pulses were always present. WOLFGANG and LIBBY [2] found that hydrogen quenched with an ethylene-argon mixture gave large plateau slopes, especially for counting at high pressures. BROWN *et al.* [3] found they had to use an external quench unit to obtain good plateaux for the counting of hydrogen at high pressures.

One of the causes of a finite plateau slope is the formation of spurious pulses due to insufficient quenching of positive ions and also the presence of metastable atoms.

CURRAN and RAE [4] have shown that spurious pulses can often amount to quite a large percentage of the count rate; and FRANEAU *et al.* [5] have shown that the number of spurious pulses formed increases linearly with the overvoltage — that is, the operating voltage minus the threshold voltage.



The effect of spurious pulses on counting rates is greatly increased when an anticoincidence ring is used to shield the counter from cosmic-ray mesons, etc. Consider, for instance, a counter which, when placed inside an anticoincidence ring, gives a total count rate of 100 cpm and a true anticoincidence count rate of 4 cpm. Suppose then that 2% of the pulses give rise to spurious pulses which are delayed longer than the paralysis time in the counting circuit. The anticoincidence count rate would be increased from 4 cpm to 6 cpm, an increase of 50%.

The reduction of spurious counts to a minimum is therefore most important in low count-rate anticoincidence shielded counters. The number of spurious counts can be kept to a minimum by:

- (a) the use of efficient quenching gas;
- (b) operation at a point relatively low down on the plateau, compatible with constant pulse height;
- (c) the use of a long paralysis time in the counting circuit (in low count-rate work this is no disadvantage); and
- (d) the use of a fast external quenching circuit.

#### 4. The characteristics of different quenching gases

Table I shows the results of tests carried out on a number of possible quenching gases. A good quenching gas needs to have an ionization potential below that of the primary gas and below any metastable levels of the primary gas. The properties of various counting gases have been published by SHARPE and TAYLOR [6] and BROWN [7], and their data was used as a guide in the selection of possible quenching agents. The gases tested represent compounds that seemed suitable and were also available. Since for adequate quenching something like 10–20% of a quenching gas is needed in a counting mixture, only those compounds with a relatively high vapour pressure were selected, because we are interested in counting at pressures of 40 cm of Hg or greater. For this reason we did not initially test toluene; but, after reading how successfully it was used by CAMERON and PUCKETT [8], we carried out some tests on it, and the results are included in Table I for comparison.

The procedure adopted was to fill two counters, each with a different quenching gas plus hydrogen and, in some cases, argon. The counters were then coupled to their counting circuits at the same pulse-height setting in both cases. The pulses were then in turn examined visually on an oscilloscope, the inspection being made at a number of points on the plateau by variation of the pulse-height setting.

In cases where the number of spurious pulses was large or the quenching action definitely inferior no further tests were made. Those quenching gases which on visual inspection seemed suitable were further tested for suitable plateau slopes and background count rates.

It can be seen from Table I that measurements were made with and without argon present in the counting gas mixture. Argon was found to have little effect, except to increase the operating potential by its presence. Therefore, argon-free mixtures were used in the later work.

The ionization potentials shown in Table I were taken from the recent, very extensive compilation made by KISER [9]. It can be seen that, on the whole, the compounds with the lower ionization potentials give the better quenching. Kiser's table shows that the methyl and ethyl secondary and tertiary amines and also some of the hydrazines have ionization potentials down to 7.5 eV. Since these compounds

also have suitable vapour pressures at room temperature, they may have better quenching properties than do ethylamine or toluene.

TABLE I  
CHARACTERISTICS OF QUENCHING GASES

Compound	Filling pressures — Quencher/Argon H <sub>2</sub> (cm of Hg)	
Benzene Ionization-Potential = = 9.3 eV	6-10-40 4-10-40 7-7-38 7-10-36 5-0-40	The quenching looked quite good on the oscilloscope. The background rate for counter No. 1 was 3.8 at a pulse-height setting of 40 V.
Ethylbromide Ionization-Potential = = 10.5 eV	6-10-38 0.6-8-39	This gave much reduced counting rates — both coincidence and anti-coincidence. This is probably due to the reduction of the counting volume to a small region around the anode, which was found to occur in ethylene dibromide quenched counters, by MATEOSIAN and FRIEDMAN [10].
Ethyl Ether Ionization-Potential = = 9.5 eV	7-10-36 5-0-40	This appeared to give good quenching with very few secondary pulses and a relatively long plateau. At pulse heights below 30 V the pulses often varied in height, showing that in many cases the Geiger discharge was not fully developed.
Hexane Ionization-Potential = = 10.1 eV	7-9-37	Very many multiple pulses, as bad as or worse than ethylene.
Iso-Propyl-amine Ionization-Potential = = 8.7 eV	7-10-36	Good quenching and good plateau but looked slightly inferior to ethylamine.
Isoprene Ionization-Potential = = 8.8 eV	7-10-36	Good quenching but looked inferior to ethylamine.
Ethylamine Ionization-Potential = = 8.8 eV	7-10-36 4-6-40 5-0-40 7-0-40 3-0-40	Very good quenching — very few multiple pulses. Had a long plateau — about 500 V.
Toluene Ionization-Potential = = 8.8 eV	1.5-0-40 2.2-0-40	Very good quenching — similar to ethylamine at 1.5 cm Hg pressure, but superior at a pressure of 2.2 cm.

### 5. Characteristics of ethylamine as a quenching gas

The quenching gases included in Table I gave better quenching characteristics than does ethylene in all cases except hexane and ethyl bromide. Toluene and ethyl amine both gave starting voltages, some 200 V lower than ethylene, at similar pressures. With hydrogen at a pressure of 40 cm of Hg, an ethylamine (5 cm Hg) quenched counter had very similar characteristics to one quenched with 1.5 cm of Hg of toluene. A counter filled to 2.2 cm of Hg with toluene looked superior to the above when the pulses were viewed on the oscilloscope, but the plateau characteristics were very similar.

It was decided to use ethylamine at a pressure of 5 cm of Hg for quenching our counters for the routine counting of tritium. It has the advantage of a high vapour pressure — 760 cm of Hg at 16°C — and so is easily pumped out of the vacuum system. It can also be stored in gaseous form in a flask on the vacuum system (which is very convenient for routine use).

The dotted curves in Fig. 3 show the anticoincidence background rate in counters No. 1 and 2 quenched with ethylamine; a mixture of 5 cm of ethylamine and 40 cm of hydrogen was used. Some curves for counter No. 4 are shown in Fig. 4, which

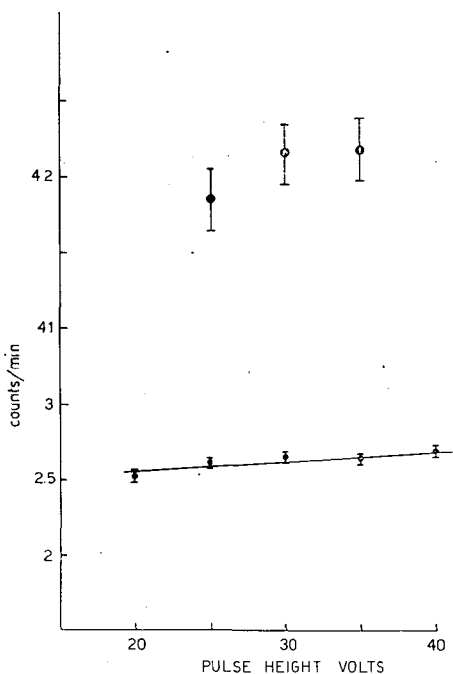


Fig. 4

Anticoincidence background and sample plateaux.

gives the background and a sample count. The curves for counter No. 5 are almost identical to those for No. 4. The lowered background for these two counters is attributed to the materials used in construction; for instance, non-lead solder was used throughout. The lowered plateau slope for counters 4 and 5 is probably due

to the use of much cleaner cathode surfaces. These surfaces were cleaned in dilute nitric and then dilute sulphuric acid solutions and finally washed with distilled water.

The cathodes of counters No. 1 and 2 had somewhat uneven surfaces. The paralysis time in our counting circuits is 15 msec, which gives rise to a correction of some 3% for the count rates that we are interested in. Counters No. 4 and 5 have now been used continuously for six months for the counting of the tritium in hydrogen gas samples, with ethylamine as a quenching gas. Over this period of time the anticoincidence background rate and its slope have not measurably changed.

## 6. Effects of impurity gases

Some tests on the effects of water vapour, nitrogen and oxygen on counting action were made. Water vapour was found to have no effect on counter action, pressures up to 8 mm of Hg being tested. However, one millimeter of air was sufficient to reduce the plateau length by 150 V and to increase the number of spurious counts. The counters still had plateaux with 4 mm of air present although they were fairly short and the number of spurious pulses was fairly large. On separate testing of the effect of oxygen and nitrogen impurities, it was found that the spurious pulses were practically all caused by the oxygen impurity. The nitrogen impurity had little effect on the counters at the bottom end of the plateau, but its presence reduced the plateau length considerably.

## ACKNOWLEDGEMENTS

I would like to thank W. J. McCabe of this laboratory for constructing counters No. 3 and 4 and also J. E. R. Penman for making many of the measurements.

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## DISCUSSION XXIII

**H. Suess** (United States of America): At present Mr. Bainbridge is not working in New Zealand but at the University of California in La Jolla, where the method he is using is not the one he has just described. Would it be possible for him to describe the method he is using at La Jolla?

**A. Bainbridge** (New Zealand): At La Jolla we have developed a method for the synthesis of ethane from hydrogen that can be used for the counting of low-level tritium activity. The reaction procedure is simple and involves the mixing of hydrogen with acetylene over a palladium catalyst. The counting characteristics of ethane are found to be ideal because of the low, flat plateaux found even at 3 atm

of pressure. With a counter having an effective volume of 1 l filled to 3 atm of ethane, not more than a tenfold tritium enrichment is necessary in order to obtain a sensitivity of 0.45 cpm per T.U. and this is sufficient for the survey of natural tritium in surface waters. The whole reaction takes no more than 4 h and two samples per day can be analyzed.



# RAPID ASSAY OF TRITIUM-LABELLED SUBSTANCES IN GEIGER-MÜLLER GAS COUNTING TUBES

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Abstract — Résumé — Аннотация — Resumen

**Rapid assay of tritium-labelled substances in Geiger-Müller gas counting tubes.** A relatively simple and rapid method is described for the measurement of relative specific activities of tritium-labelled solid substances, principally for the determination of low-level activities of small samples.

The measurement of radioactivity is accomplished by means of acetylene in Geiger-Müller internal gas counting tubes. Tritium-labelled solid samples are oxidized on products of thermal decomposition of silver and potassium permanganates, used for the retention of carbon dioxide or sulphur dioxide and oxides of nitrogen simultaneously. Water vapour in a stream of nitrogen is passed directly through a layer of finely ground technical calcium carbide. The acetylene evolved is condensed in the attached counting tube. The maximum partial pressure of acetylene for suitable self-quenching mixtures with argon is 8 cm Hg.

The procedure described permits preparations and fillings of up to 18 samples during 8 h in one line for activities up to the order of  $10^4 \mu\text{c}$ . The background reduction of the counting tubes used, with volumes of about 60 ml, permits short and routine measurements of sample activities up to  $8 \mu\text{c}$ . This method makes possible reproducible measurements of relative specific activities of solid tritium-labelled substances with a maximum total error of less than  $\pm 5\%$  when the standard deviation of counting is less than  $\pm 2\%$ .

**Dosage rapide de substances tritiées dans des tubes Geiger-Müller à gaz interne.** Les auteurs décrivent une méthode assez simple et rapide pour mesurer les activités spécifiques relatives de substances solides tritiées, principalement en vue de déterminer les faibles et très faibles activités de petits échantillons.

On mesure l'activité après transformation de la substance en acétylène, dans des tubes compteurs Geiger-Müller à gaz interne. L'oxydation des échantillons solides tritiés se fait sur un mélange de produits de la décomposition thermique des permanganates d'argent et de potassium, utilisés pour la fixation simultanée de l'anhydride carbonique ou de l'anhydride sulfureux et des oxydes d'azote. La vapeur d'eau entraînée par un courant d'azote passe directement à travers une couche de carbure de calcium commercial en poudre fine. L'acétylène qui se dégage se condense dans le tube de comptage relié au montage. La pression maximum partielle de l'acétylène est de 8 cm de mercure pour les mélanges autocoupeurs appropriés à base d'argon.

La méthode indiquée permet de préparer et d'introduire dans le même appareil jusqu'à 18 échantillons pendant une période de huit heures pour des activités allant jusqu'à  $10^4 \mu\text{c}$ . La réduction du mouvement propre des tubes compteurs utilisés — pour un volume d'environ 60 ml — permet de mesurer rapidement et couramment des échantillons d'une activité de  $8 \mu\text{c}$ . La méthode décrite permet de doser avec une bonne reproductibilité les activités spécifiques relatives de substances solides tritiées, l'erreur totale maximum étant inférieure à  $\pm 5\%$  lorsque l'écart type de comptage est inférieur à  $\pm 2\%$ .

**Быстрый анализ меченных тритием веществ в газовых счетчиках Гейгера-Мюллера.** Описывается сравнительно простой и быстрый метод для измерения относительной удельной активности меченных тритием твердых веществ, главным образом для определения более слабых и низкого уровня активности небольших проб.

Измерение радиоактивности производится по ацетилену внутри газовых счетчиков Гейгера-Мюллера. Меченные тритием пробы из твердого вещества

окисляются в продукты теплового разложения серебряных и калиевых перманганатов, используемых для удержания одновременно двуокиси углерода или двуокиси серы и окиси азота. Водяной пар в потоке азота проходит непосредственно через слой технического мелкозернистого карбида кальция. Выделяющийся ацетилен конденсируется в присоединенном счетчике. Максимальное парциальное давление ацетилена для подходящих самочасящихся смесей с аргоном равняется 8 см. рт. ст.

Описанная процедура позволяет готовить и заполнять до 18 образцов в течение 8 часов на одной линии для активности до  $10^4$   $\mu$ с. Уменьшение величины фона используемых счетчиков с объемом около 60 мл позволяет быстро и просто измерять активности проб до 8  $\mu$ с. Описанный метод делает возможным воспроизводимые измерения относительно удельной активности меченных тритием твердых веществ с максимальной общей погрешностью менее чем  $\pm 5\%$ , когда стандартное отклонение счетчика менее чем  $\pm 2\%$ .

#### **Análisis rápido de sustancias tritadas en el interior de tubos Geiger-Müller para gases.**

Para la medición de las actividades específicas relativas de sustancias sólidas marcadas con tritio, los autores describen un método bastante sencillo y rápido que resulta especialmente adecuado para determinar actividades reducidas de muestras pequeñas.

Luego de transformar la sustancia en acetileno, la medición de la radiactividad se efectúa en tubos contadores Geiger-Müller de gas interno. Las muestras sólidas marcadas con tritio se oxidan en presencia de una mezcla de productos de descomposición térmica de los permanganatos de plata y potasio, utilizados para fijar simultáneamente el anhídrido carbónico o el anhídrido sulfuroso y los óxidos de nitrógeno. Se hace pasar directamente vapor de agua arrastrado por una corriente de nitrógeno a través de una capa de carburo de calcio comercial finamente molido. El acetileno que se desprende se condensa en el tubo contador conectado al aparato. La máxima presión parcial del acetileno en mezclas con argón apropiadas para la autoextinción es de 8 cm de mercurio.

El procedimiento descrito permite, en el plazo de 8 horas, preparar e introducir en el mismo aparato hasta 18 muestras de  $10^4$   $\mu$ curies de actividad. Gracias a la reducción del fondo de los tubos contadores usados — de un volumen de 60 ml aproximadamente — es posible efectuar mediciones breves y corrientes de muestras de 8  $\mu$ curies. El método descrito permite determinar con una reproducibilidad satisfactoria las actividades específicas relativas de sustancias sólidas marcadas con tritio con un error máximo total inferior a  $\pm 5\%$ , cuando la desviación standard del recuento es inferior a  $\pm 2\%$ .

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The problem of measuring low activities arises during application of tritium-labelled compounds in tracing experiments. Autoradiography is by virtue of its special character applicable only to the solution of special problems [1]; the application of a window-less flow counter is limited because of self-absorption, which does not permit measurements of low specific activities [2]. In addition, the substances used in the different fields of chemistry, and particularly biology, are sometimes of such character as to complicate considerably the preparation of samples for measurement in window-less or liquid scintillation counters [3]. In the latter case, another difficulty arises: during measurement, some substances cause quenching in the scintillator [4]. These shortcomings are eliminated by measurement of the radioactivity of samples introduced into an internal counting tube in the gaseous phase [5, 6, 7, 8]. Such methods require, however, a relatively laborious preparation of samples.

The present paper describes a procedure for speeding up of the preparation of the sample with relatively simple equipment. This speeding up is made possible by a special oxidation of the tritium-labelled compounds and a direct passage of the water vapour formed through a layer of calcium carbide to form acetylene.



The preparation and filling of acetylene into the counting tube is carried out continuously on a single line. The procedure described makes it simultaneously possible to lower considerably the contamination of the apparatus.

### Experimental procedure

The procedure consists of two parts: preparation of acetylene and its filling into the Geiger-Müller internal gas counting tube, and the actual radioactivity measurement.

The first part of the filling arrangement intended for oxidation of organic substances is shown in Fig. 1. The sample placed on a platinum planchet is introduced

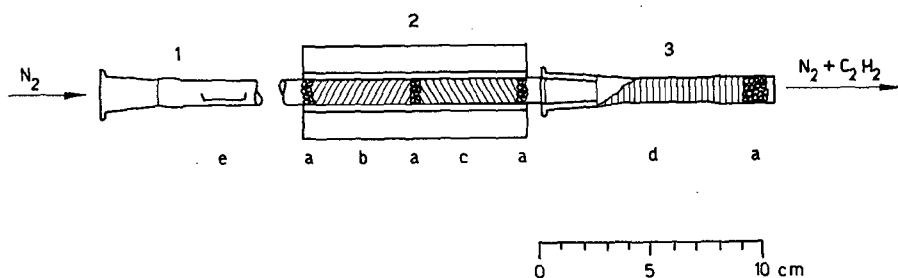


Fig. 1

The preparation of acetylene.

1 Combustion tube; 2 Furnace; 3 Tube with  $\text{CaC}_2$ ; a Glass wool; b Product of thermal decomposition of  $\text{AgMnO}_4$ ; c Product of thermal decomposition of  $\text{KMnO}_4$ ; d  $\text{CaC}_2$ ; e Platinum planchet with sample.

into a quartz tube 10 mm in diameter. Oxidation is carried out in a stream of light-bulb-type nitrogen on about 50 mm layers of the products of thermal decomposition of silver and potassium permanganates [9, 10, 11]. The former also serves to trap sulphur dioxide, halogens, phosphorus and arsenic; the latter, to absorb carbon dioxide and oxides of nitrogen. The 50 mm layer will trap quantitatively 3 mM  $\text{CO}_2$ . Both oxidizing agents are separated by loose plugs of glass wool and are heated electrically to  $550^\circ\text{--}580^\circ\text{C}$ . The actual combustion of the sample is achieved by slow heating of the whole tube to dull red heat. This procedure will take about 10 min for samples weighing about 10 mg. In the course of a further four to five min the heating to dull red heat is repeated twice. Directly behind the electric furnace the combustion tube is taper-joined to a quartz tube filled with a layer about 50 mm in length of finely powdered technical calcium carbide. Water vapour formed during combustion is conducted directly into this layer, where it reacts with calcium carbide, giving rise to acetylene. The technique of combustion with oxidizing agents in a stream of nitrogen makes it possible to use liquid nitrogen for quantitative trapping and transfer of acetylene; this eliminates the risk of contamination of the contents of the counting tube by traces of electronegative oxygen [12].

In the following part of the filling line (Fig. 2) acetylene is condensed in a spiral trap immersed in liquid nitrogen. After oxidation and trapping of acetylene, a stopcock at the end of the first part of the line intended for the preparation of acetylene is closed. The carrier nitrogen is then evacuated and acetylene transported under vacuum of the order of  $10^{-4}$  mm Hg by means of liquid nitrogen to

the cold finger of the measuring space. The pressure of the sample is recorded after expansion on an attached U-tube manometer filled with silicone oil. The sample is frozen in the cold finger of the counting tube, which is then filled with argon from an attached reservoir. The counter (about 60 ml in volume) is made

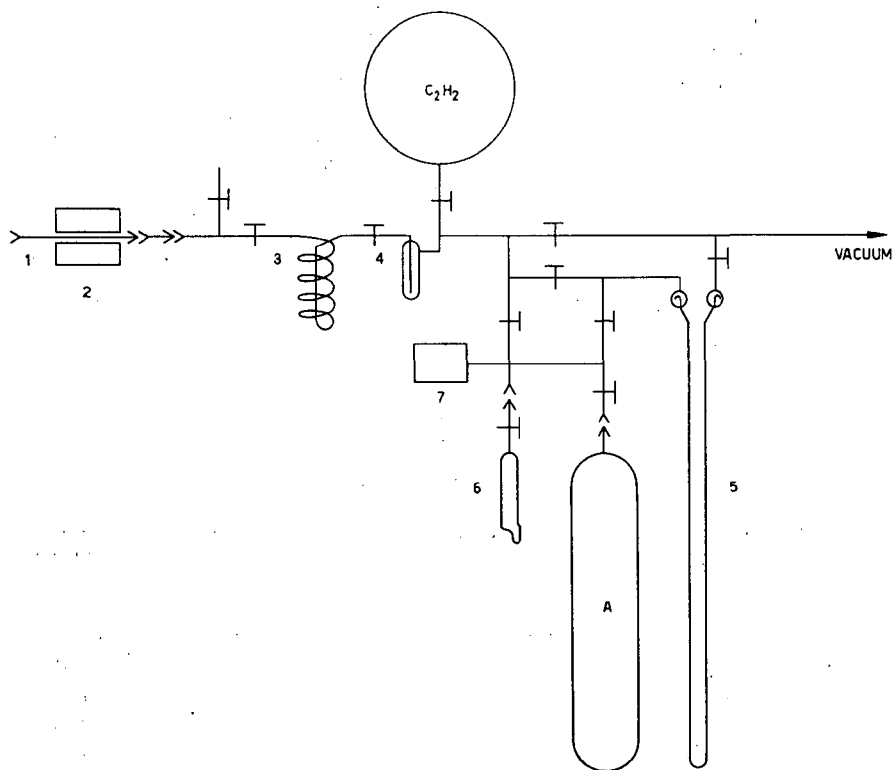


Fig. 2

Scheme of the filling line with G-M counter.

1 Combustion; 2 Furnace; 3 Spiral trap; 4 Trap in the measuring space; 5 U-tube manometer with silicone oil; 6 G-M internal gas counting tube; 7 Penning gauge.

of a brass tube with sealed glass ends [13]. If the partial pressure of acetylene after filling is between 10 and 80 mm Hg and that of argon between 95 and 140 mm Hg, the working voltage of the self-quenching counters is less than 2 kV. With the above pressure range, the counters employed have plateaux of 250–500 V with slopes less than 3% per 100 V; the dead time is  $310 \pm 70 \mu\text{s}$ . The entire procedure from insertion of the solid sample into the combustion tube to the end of filling of the counter tube does not take more than 25 to 30 min.

Radioactivity measurement must be commenced not earlier than 20 to 25 min after filling the counting tube. Measurement of low activities is carried out in a steel box with a closed ring of screening G-M counters connected with the internal gas counter in anticoincidence [13]. The background inside this arrangement is suppressed below 5 counts/min. This reduction of background permits short and routine measurements of sample activities up to  $8 \times 10^{-6} \mu\text{c}$ .

## Results and discussion

Quantitative conversion of the sample into acetylene and its transfer into the counting tube was estimated by comparison of the pressure measured by the manometer with pressures calculated from the weight of the sample, with correction for room temperature. It follows from Table I that the conversion of the solid sample

TABLE I  
CALCULATED AND MEASURED PRESSURES OF ACETYLENE FROM VARIOUS COMPOUNDS

Sample	Pressure		Deviation (%)
	calculated oil (mm)	found oil (mm)	
Benzoic acid	52.1	52.0	- 0.2
	143.0	142.5	+ 0.3
Lactose	39.7	39.0	- 1.8
	98.3	97.25	- 1.0
5-bromouracil	32.6	32.75	+ 0.5
	102.7	101.75	- 1.0

to acetylene and its transport into the measuring space is quantitative and fully reproducible. The quantitative character of acetylene transfer from the measuring space into the counting tube was confirmed by measurement of the pressure after retransfer of the same sample from the tube into the measuring space. The manometer pressures were read with an accuracy of  $\pm 0.25$  mm silicone oil.

The relationship between the amount of sample and measured activity was then investigated. As Fig. 3 shows, this relationship is linear. The deviations of the values of specific activity deduced from our measurements is less than  $\pm 3.5\%$  of their mean when the standard deviation of counting (SD) is less than  $\pm 2\%$ . The activities were determined from the measured counting rates on the assumption that the acetylene contains half the activity of the sample; the average yield of radioactivity measurement was derived from the geometry of the counting tube and verified by means of the standard.

In the measurement of greater series of samples special attention was devoted to elimination of residual activity [14]. This was estimated by measurement of the activity of acetylene obtained by oxidation of an inactive sample. After combustion of the sample with activity up to  $0.01 \mu\text{C}$  the repeated heating of the combustion to red heat (under passage of nitrogen), as described, is sufficient to remove the possible contamination. As shown in Table II the memory effect does not come into play in the other parts of the line so that before oxidation of another sample it is only necessary to exchange the tube with calcium carbide. In this case the procedure described permits preparation and filling of up to 18 samples during eight hours in one line. Samples with activity of less than  $0.1 \mu\text{C}$  contaminate only the combustion tube, while at higher activities active acetylene itself also causes contamination. The removal of the contamination in the combustion tube was

TABLE II  
MEMORY EFFECT IN THE FILLING LINE AND IN THE COUNTER

Sample activity ( $\mu\text{c}$ )	Memory effect	
	of the whole line (cpm)	due to acetylene (cpm)
0.01	—	—
0.05	$3.8 \pm 0.4$	—
0.1	$10.8 \pm 1.1$	$< 1$
0.2	$19.8 \pm 2.0$	$2.3 \pm 0.2$
1.1	$104.3 \pm 10.4$	$20.6 \pm 2.1$

achieved by the heating of a few drops of water at the beginning of the tube in a stream of nitrogen with simultaneous repeated heating of the tube to red heat. For removing the contamination due to radioactive acetylene it is usually sufficient to flush the line and the tube three times with inactive acetylene with evacuation to about  $10^{-5}$  mm Hg. The decontamination procedure does not require more than 15 min.

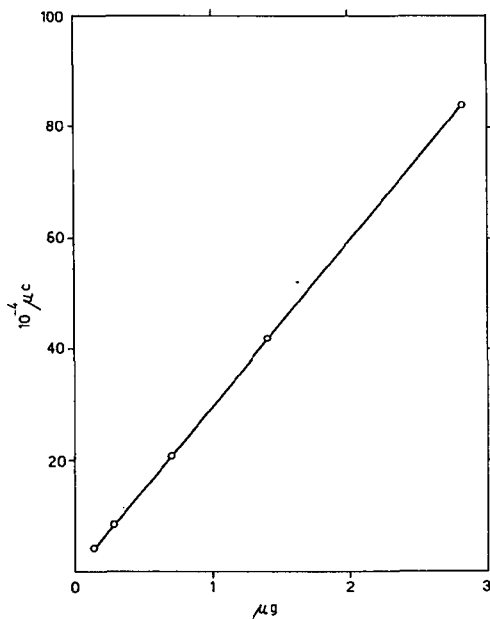


Fig. 3

The linearity and reproducibility of the assay ( $\text{SD} \pm 2\%$ ).

It follows from our experiments that, for suppression of the memory effect, it is of advantage to reduce the area which comes into contact with active water and to convert this water to acetylene as quickly as possible.

In order to speed up the procedure even more it is recommended to set up the first part of the arrangement twice in parallel. In this case it is then possible to carry out oxidation in one part while preparing the other for oxidation of a subsequent sample.

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## DISCUSSION XXIV

W. F. Libby (United States of America): Has Mr. Grünberger had any explosions?

D. Grünberger (Czechoslovakia): No, we did not, and we have been using these methods in our laboratories for a number of years. We have also been using them for the analysis of organic, unlabelled compounds.

J. Eastham (United States of America): How often did the speaker have to change the calcium carbide tube when preparing the acetylene?

D. Grünberger: The calcium carbide tube must be changed after each combustion.

J. Eastham: As regards the fractionation in your reaction, it seems to me that you lose at least 50% of your activity due to the chemical nature of the reaction and perhaps more due to the isotope effect.

D. Grünberger: Yes, you are right. The chemical yield is 50%. Our efficiency of measurement is about 30%. As I have said, this method is a relative one and is sufficient for biochemical purposes.

J. Hasan (Finland): Had Mr. Grünberger any difficulty in condensing the acetylene quantitatively with liquid N<sub>2</sub> from gaseous N<sub>2</sub> at or near atmospheric pressure?

D. Grünberger: The condensation was very easy: the nitrogen was pumped off and we never had any losses. We encountered no difficulties.



# A ZINC FUSION METHOD FOR THE DETERMINATION OF TRITIUM IN BIOLOGICAL MATERIAL BY GAS COUNTING

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Abstract — Résumé — Аннотация — Resumen

**A zinc fusion method for the determination of tritium in biological material by gas counting.** The conversion of organic compounds to a mixture of hydrogen and methane by mixture with metallic zinc and suitable catalysts offers a convenient means for the determination of tritium in organic material by gas assay. It has been found, however, that, at least in proportional counting, compounds of certain types do not give reliable results with this method; and when a trial of its application to animal tissues was made, the results were extremely inaccurate.

As the principle seemed to offer several advantages over other published methods, a search was conducted for reagents which would render it usable with biological material. It was found that, when up to 10 mg of animal tissue, such as blood, muscle and liver, containing or mixed with various tritiated compounds were heated for 3 h at 650°C in an evacuated and sealed tube of special glass together with sufficient amounts of metallic zinc powder, nickel oxide and anhydrous sodium carbonate, gas which could be assayed in brass cathode proportional counters filled to atmospheric pressure with inactive methane was produced. Above 4000 V the counters filled with this gas mixture exhibited plateaux several hundred volts long and with a slope less than 1% per 100 V.

This method for conversion of biological material to a suitable gas for proportional counting was found to be readily reproducible with a mean accuracy of within better than 3%. No serious memory effects have been noted, even with samples of rather high specific activity.

**Méthode de fusion au zinc pour le comptage en phase gazeuse du tritium contenu dans des substances biologiques.** La transformation de composés organiques en un mélange d'hydrogène et de méthane, par chauffage avec du zinc métallique et des catalyseurs appropriés, est un moyen commode de faire la détermination quantitative du tritium contenu dans des substances biologiques par comptage, en phase gazeuse. On a constaté cependant, tout au moins lorsqu'on utilise le comptage proportionnel, qu'avec certains composés les résultats obtenus ne sont pas dignes de foi; lors d'un essai sur des substances biologiques, les résultats ont été même d'une grande inexactitude.

Comme le principe semble présenter plusieurs avantages par rapport à d'autres méthodes connues, on a recherché quels réactifs pourraient permettre de l'appliquer aux substances biologiques. L'auteur s'est servi d'un tube scellé en verre spécial dans lequel il a fait le vide; dans ce tube, il a chauffé à 650°C pendant trois heures une quantité inférieure ou égale à 10 mg de tissu animal — sang, muscles ou foie — contenant des composés tritiés ou la même quantité d'un mélange de tissu animal et de composés tritiés après avoir introduit dans le tube une quantité suffisante de zinc métallique en poudre, d'oxyde de nickel et de carbonate de sodium anhydre; il a constaté qu'il se produisait un gaz qui peut être analysé dans des compteurs proportionnels à cathode de laiton remplis de méthane inactif à la pression atmosphérique. Au-delà de 4000 volts, les compteurs remplis de ce mélange gazeux donnent des paliers longs de plusieurs centaines de volts et dont la pente est inférieure à 1% par 100 volts.

Il est à noter que par cette méthode de transformation de la substance biologique en un gaz approprié pour le comptage proportionnel, les résultats peuvent être reproduits avec une exactitude moyenne meilleure que 3%. L'auteur n'a pas constaté d'effets de mémoire importants, même avec des échantillons d'une activité spécifique assez élevée.

**Метод плавления цинка для определения количества трития в биологическом материале при помощи дозиметрии газа.** Превращение сложных органических соединений в смесь водорода и метана с подмешиванием металлического цинка

и использованием подходящих катализаторов может служить подходящим методом определения при помощи анализа образующихся газов количества трития в органических материалах. Однако было обнаружено, что, по меньшей мере при использовании пропорциональных счетчиков, некоторые сложные соединения не дают по этому методу надежных результатов, а когда была сделана попытка применить этот метод к тканям животных, то получились чрезвычайно неточные результаты.

Поскольку этот принцип может дать, по-видимому, целый ряд преимуществ по сравнению с другими опубликованными методами, было произведено исследование для нахождения реагентов, которые позволили бы применять этот метод для биологического материала. Было обнаружено, что если взять до 10 миллиграммов ткани животных, как, например, крови, мышц или печени, содержащих различные тритированные сложные соединения или смешанные с ними, и если подогревать их в течение трех часов при 650 °C в герметически закрытой вакуумной трубке из специального стекла в присутствии достаточного количества металлического порошка цинка, окиси никеля или безводного углекислого натрия, то образуется газ, который может быть проанализирован пропорциональными счетчиками с латунным катодом, наполненными находящимся при атмосферном давлении неактивизированным метаном. При напряжении свыше 4000 вольт наполненные этой газовой смесью счетчики указывали на наличие плато на протяжении нескольких сотен вольт с наклоном менее чем в 1% на 100 вольт.

Было установлено, что этот метод превращения биологического материала в подходящий для пропорционального отсчета газ легко воспроизводим и дает среднюю погрешность менее, чем на 3 процента. Даже с образцами довольно высокой удельной активности не наблюдалось явлений сколько-либо заметного ее искажения памятью аппарата.

**Método de fusión con zinc para el recuento en fase gaseosa del tritio contenido en sustancias biológicas.** La transformación de compuestos orgánicos en una mezcla de hidrógeno y metano por calentamiento con zinc metálico y catalizadores adecuados constituye un medio cómodo de determinar por recuento en fase gaseosa el tritio contenido en sustancias orgánicas. Sin embargo, se ha comprobado que, por lo menos cuando se recurre al recuento proporcional, determinados compuestos no dan resultados fidedignos y cuando se procuró aplicar el método a tejidos animales, los resultados obtenidos fueron extremadamente inexactos.

No obstante, como el principio parece ofrecer varias ventajas con respecto a otros métodos conocidos, se llevó a cabo una búsqueda de reactivos susceptibles de facilitar su aplicación a las sustancias biológicas. Se comprobó que, si se calientan hasta 10 mg de tejidos animales (sanguíneo, muscular o hepático) que contengan o vengan mezclados con diversos compuestos trititados, durante tres horas, a 650 °C, en un tubo sellado de vidrio especial en el que se ha hecho el vacío, juntamente con cantidades suficientes de zinc metálico en polvo, óxido de níquel y carbonato de sodio anhidro, se forma un gas que se puede analizar en contadores proporcionales de cátodos de latón, llenos de metano inactivo a presión atmosférica. Por encima de los 4000 V, los contadores que contengan esta mezcla gaseosa presentan rellanos de varios centenares de voltios de longitud, con una pendiente inferior al 1% por cada 100 V.

Se comprobó que esa transformación de las sustancias en un gas adecuado para el recuento proporcional permite obtener resultados reproducibles con una exactitud media superior al 3%. No se han observado efectos de memoria graves, ni siquiera en el caso de muestras de actividad específica bastante elevada.

## Introduction

Despite recent developments in other methods of assay, internal gas counting still offers the most sensitive means for detecting and measuring the amount of tritium present in a sample. Most published methods for the quantitative analysis



of tritium in organic substances [1, 2] require at least two separate operations: the hydrogen in the sample is generally first combusted to water and then converted by a suitable reaction into gas to be introduced into the sensitive volume.

A procedure has been described [3, 4] by which the quantitative conversion of hydrogen in a variety of organic compounds into a gas mixture suitable for assay in an ion chamber is accomplished in a single operation by heating the sample for 3 h with metallic zinc, nickel oxide and water in a sealed tube at 640 °C. Disposable reaction tubes for heating the sample largely eliminate "memory" effects, common in gas counting; the apparatus necessary for successful performance is fairly simple and the vacuum easily produced.

The mixture of hydrogen and methane produced in the conversion of some organic compounds by this method has been found suitable for measurements in glass-walled proportional counters [5]; in general these counters seem to be more practical than ion chambers for low-level determinations. The former are, however, much more sensitive to variations in gas composition, and although it was found originally [3] that the conversion of many compounds yielded only hydrogen (28%) and methane (72%), significant amounts of benzene and ammonia have also been found to be produced when urea and aromatic halides, respectively, were heated in the above manner. Compounds containing primary amino groups have also been found to give inaccurate results when the zinc fusion method is applied to proportional counting [6], and this method has been reported to be "totally useless" for ammonium salts.

It thus appeared somewhat questionable whether the method would be satisfactory for the direct analysis of tritium in crude products of animal origin, e. g. pieces of tissue. As the principle, nevertheless, seemed to offer several advantages over other published methods an attempt was made to apply it to biological material [7].

## Experimental

A "Supremax" or Jena glass with an internal diameter of 9–11 mm and an unbreakable tip was used to heat a number of elements. They included 1 to 10 mg of animal tissue such as blood, muscle and liver and amounts weighing 1 to 10 mg of alpha-labelled H<sup>3</sup>-myristic acid, H<sup>3</sup>-glucose and H<sup>3</sup>-fructose (normally labelled), H<sup>3</sup>-phenylalanine (labelled in the benzene ring), H<sup>3</sup>-progesterone, H<sup>3</sup>-thymidine and tritiated water. They were mixed with 1.5 g of zinc powder or zinc granules, 150 mg of nickel oxide and 5 mg of water. The total amount was sealed in the evacuated tube and heated for various periods of time up to 4 h. The tubes were kept horizontally in a furnace at 650 °C. Alternately, double or triple determinations were performed on homogenates of tissues from animals injected with tritiated substrates. It has been claimed [6] that only the original type of nickel oxide used by WILZBACH *et al.* [4] has yielded useful results with the zinc fusion method and therefore only this reagent was used (Nickel Oxide, Black Powder, Item 1-2792 by J. T. Baker Chemical Co., New Jersey).

The tubes were broken by tipping and the gas produced with heating was expanded into 150 ml brass cathode counter tubes (Firma Prof. Berthold, Wildbad, Black Forest) in a vacuum apparatus (Fig. 1) similar to that described by WILZBACH *et al.* [4]. The counters were filled to atmospheric pressure with inactive methane and connected to a preamplifier (Frieske and Hoepfer 40699/51). The output pulses were fed into a fast scaler (Ekco Automatic Scaler, Type N 530 F) and a separate stabilized high-voltage source (Frieske and Hoepfner FH 487) supplied the counters with up to 4500 V. Activity measurements were made by counting

10 000 pulses at several points between 3000 and 4500 V to determine plateau characteristics of the fillings.

Reproducible results could not be obtained with this reaction mixture even after heating for 4 h and doubling the amount of reagents. Differences of several hundred

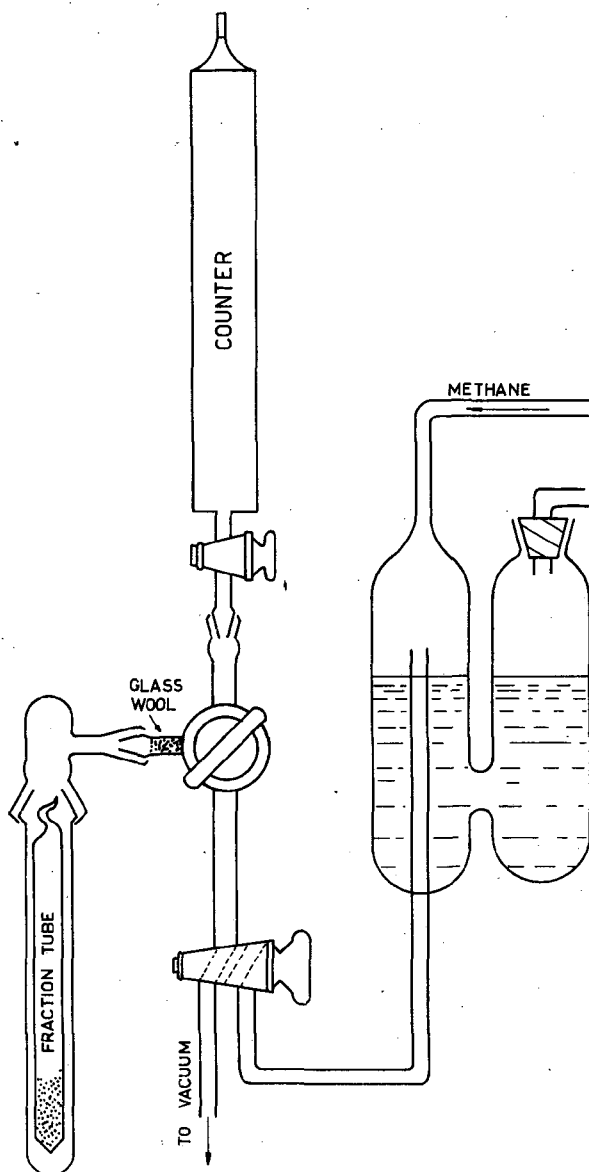


Fig. 1

Apparatus for breaking reaction tube and filling counter with gas from reaction and/or inactive methane. Scale: Length of reaction tube 15 cm. After WILZBACH *et al.* [3].

per cent were measured in duplicate determinations and the correlation between known and found specific activities was correspondingly poor. A liquid was sometimes seen to condense in the thin-walled break-tips of the reaction tubes during cooling, but this was not apparent after the tubes had attained uniform room temperature. This, together with occasional contamination of counters suggested the presence of water. Amalgamating the zinc with mercury did not improve the results, but when no water was initially added all memory effects disappeared and the variability, diminished a little, even if not to within practical limits.

As facilities for analyzing the reaction products were not available, a number of reagents were tried more or less haphazardly. It seemed fair to suppose that interfering substances in the tissues were more likely to cause disturbances than incomplete disintegration of the labelled compounds. Previously published observations [4, 6], the known approximate composition of tissues and fundamental counter characteristics [7] all suggested reaction products of nitrogen or sulphur as the most probable sources of interference with counter operation. A method has been described [8] for the quantitative determination of sulphur, nitrogen and halogens in an organic sample, where the compound to be analyzed is heated with a flame in a mixture of zinc powder and sodium carbonate. It is claimed that this procedure will convert quantitatively the sample nitrogen into sodium cyanide, sulphur into zinc sulphide and halogens into halides. The exact temperature is not given but the test tube containing the mixture should finally be "glowing red". The reaction thus seemed to offer a means for preventing the substances mentioned above from being introduced into the counter.

Samples of animal tissue mixed with or incorporating labelled compounds, as related above, were now heated and analyzed in a similar manner, using varying amounts of zinc powder or granules together with 50 to 1500 mg of anhydrous sodium carbonate and 150 mg of nickel oxide as the reaction mixture. Satisfactory results were regularly obtained by heating the reaction tubes for 3 h at 650°C when sufficient amounts of zinc and sodium carbonate were present in the mixture. It was furthermore found that (a) a variety of zinc powders (not necessarily free of arsene) gave more reproducible results than coarse granules; (b) amalgamating the zinc with mercury did not improve accuracy or yield; (c) the absence of nickel oxide did not affect the results in the range studied.

For comparison, several samples were also analyzed by the method of GLASCOCK [1] previously used in this laboratory, where samples were first combusted to water which was then converted to butane by reacting with *n*-butyl magnesium bromide reagent. The butane was assayed in glass-walled, stainless steel cathode Geiger counters. Half of the tritium was lost in the Grignard reaction.

## Method

Up to 15 mg of biological material was weighed accurately and placed, together with 500 mg of anhydrous sodium carbonate and 2 g of zinc powder, in a 17–20 cm tube of "Supremax" glass (Jena) (or "Pyrex" 1720) with an internal diameter of 9–11 mm and a wall thickness of some 1 mm, provided at the other end with an easily breakable tip. Liquid samples were introduced in small sealed ampoules of pyrex glass with break-tips, together with some 5 mg of inactive water if the sample weight was below 1 mg. The tube was constricted 3–5 cm from the open end, evacuated to about 1 mm Hg pressure and sealed. Ampoules for liquids were broken by violent shaking. One or several reaction tubes were each placed inside a protective metal tube and kept horizontally for 3 h in an oven at 650°C. The

heat in the furnace was evenly distributed to avoid explosions. The tubes were then taken out, allowed to cool and placed into a breaking tube in a suitably designed apparatus, e. g. the type (Fig. 1) described by WILZBACH *et al.* [4]. The tip was broken, the gas was allowed to expand into the previously evacuated counter, or it could be quantitatively transferred there by means of a Toepler pump or by flushing with inactive methane. The counter was brought to atmospheric pressure with inactive methane and connected after 5—15 min to a suitable electronic apparatus for measurement.

## Results

With the reaction mixture described above a gas was invariably obtained from various tissue samples, which contained the tritium in the sample quantitatively for at least most biological purposes, and which, with the addition of inactive methane, could be assayed for tritium content in brass cathode internal gas counters in the proportional region. The plateaux obtained above 3800—4000 V with counters filled with this mixture to atmospheric pressure were several hundred volts long with a slope of less than 1% per 100 V. Neither loss of plateau nor other counter failure has been observed as yet. Activities of up to 10 000 counts/sec have been introduced into the counters without detectable memory effect, and only one counter has suffered from permanent contamination, presumably with water.

TABLE I  
SPECIFIC ACTIVITIES OF SEVERAL TRITIUM-LABELLED COMPOUNDS  
OBTAINED BY SINGLE RANDOM DETERMINATIONS IN THREE DIFFERENT  
SYSTEMS

Labelled Compound	Specific Activity $\frac{(\text{counts/sec})}{(\text{mg})}$		
	1 Compound alone	2 Mixed with tissue	3 By combustion (x 2)
HTO	10.33	10.62	10.31
Myristic acid	37.32	36.84	35.92
Stearic acid	3.26	3.17	2.98
Progesterone	412.8	401.6	402.4
Phenylalanine	111.4	112.4	112.2
Glucose	3141	3235	—
Fructose	756.4	753.3	—
Thymidine	156.6	161.7	—

Column 1 = pure compound alone heated for 3 h with zinc powder and anhydrous sodium carbonate in an evacuated and sealed tube at 650°C; gas produced was assayed in a proportional counter filled the atmospheric pressure with inactive methane. Column 2 = compound mixed with 15 mg of dried animal tissue (blood, muscle, liver) and assayed as above. Column 3 = pure compound combusted in a stream of oxygen, combustion water converted into butane by reacting with *n*-butyl magnesium bromide for 1 h at 110°C; butane assayed in a Geiger counter. (The results are corrected for various factors of counter geometry and efficiency; half of the tritium is lost in the Grignard reaction.)

The results from several analyses of different substances as pure compounds and mixed with different tissue constituents are represented in Table I. For comparison, results for the same substances as assayed with GLASCOCK's [1] method of combustion and water-to-butane conversion have also been presented after correction for various

factors of counter geometry and counting efficiency. The agreement seems satisfactory when the loss of tritium in the Grignard reaction of the latter is taken into account. The method error came to 2.5% in the present analyses in determinations performed routinely by a non-professional girl technician at the rate of about 15 assays a day; in this connection the rather deplorable fact deserves notice, that the best balance that has been available for this work permits sample weighing with an accuracy of only 0.05 to 0.1 mg, which is bound to introduce a considerable error into the lower weight range.

No effect of sample size on the yield has been noted in the range studied, i. e., up to 15 mg of dried animal tissue. Pieces of chromatography paper and cellulose acetate electrophoresis strips weighing up to 50 mg have been successfully analyzed. With samples weighing over 20 mg, however, it is preferable to start heating gradually followed by slow cooling to avoid explosion of reaction tubes. Infinitely small samples have also been accurately assayed by introducing dilute solutions and evaporating the solvent before adding reagents, or by analyzing colonies of a few hundred Hela cells attached on cover slips. About 5 mg of inactive water has usually been added as carrier for samples weighing less than 1 mg.

No isotope effects have been noted in the method so far, neither has it been possible to confirm with certainty any retention of activity in the reaction tube as described by WILZBACH *et al.* [3, 4].

The overall efficiency of the method depends mostly on counter characteristics and on the fraction of the gas produced which is actually introduced into the counter. The 150 ml brass cathode counters seem to react to about half of the disintegrations from the tritium within them. In the present work the gas produced in zinc fusion has just been expanded or flushing into the evacuated counters from the reaction tube in the breaking tube without further pumping, introducing thus about  $\frac{3}{4}$  of the yield into the sensitive volume. With these counters, then, determinations are routinely made with an overall efficiency of about 38%. Experiments are at present made with an apparatus designed to introduce all the gas produced into the counters by flushing the heating tubes with methane. The background in the counters is some 1.4 counts/sec. Occasional batches of sodium carbonate have been found to increase the background by 0.2 to 0.4 counts/sec. This increase in background may sometimes even vary within the batch from sample to sample. No explanation has been found for the phenomenon, and such batches have been immediately discarded. No excessive background seems to develop into initially "pure" carbonate.

## Discussion

The method presented seems capable of converting the organically-bound tritium and hydrogen in animal tissues into a gas suitable for assay in brass cathode proportional counters filled to atmospheric pressure with inactive methane. The composition of the gas is unknown but volatile compounds of nitrogen, sulphur and halogens are thought to be largely excluded. Hydrogen, methane and perhaps some carbon dioxide seem likely components whereas carbon monoxide could be supposed to derange counter performance.

Sodium carbonate was added to bind nitrogen, sulphur and halogens but it might also act as a catalyst, e. g. oxidant, promoting decomposition of the sample constituents; this could explain the finding that in its presence nickel oxide seems superfluous, whereas it has been found essential for quantitative conversion in previous methods.

The accuracy obtained in routine use should suffice for most biological applications, the more so, as no isotope effects have been noted so far. Furthermore, the accuracy could probably be improved considerably by just using a microanalytical balance which has not been available for the present work.

The amount of gas produced by different sample types in the conversion reaction and its predictability have not been studied. Such a study might prove useful for improving the accuracy in the determination of specific activities, which now depend solely on the precision in weighing the sample and on the completeness of conversion.

Even the large variety of organic compounds present in animal tissues do not present definite proof for the general applicability of the present method to all organic material. Reduction, however, seems to be a basic mechanism capable of numerous variations and other modifications seem possible for the single-step zinc fusion conversion of organic hydrogen into a form suitable for gas counting.

### Summary

Heating with zinc, nickel oxide and water in a sealed tube did not yield consistent amounts of gaseous tritium measurable by proportional counting when applied to animal tissues. After various trials it was found that the hydrogen from up to 15 mg samples of tissue could be fairly quantitatively converted into assayable gas by heating them for 3 h at 650°C in sealed and evacuated tubes together with 2 g of zinc powder and 500 mg of anhydrous sodium carbonate. Brass cathode proportional counters containing this gas and filled with inactive methane to atmospheric pressure exhibited long plateaux with a slope less than 1% per 100 V.

### ACKNOWLEDGEMENTS

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### DISCUSSION XXV

J. L. Garnett (Australia): It may be of interest to mention that our research group in Sydney, Australia, also uses zinc dust instead of zinc mesh for tritium analyses by the method which Dr. Hasan has described. In so doing, we have

observed that if combusted tubes are allowed to stand for several days (e. g. over a weekend) prior to expansion and analysis, appreciable adsorption (10—20%) of the tritium on the catalyst occurs. However, if the tubes are reheated for 5 min at 650°C immediately before analysis, no such error due to adsorption effects is observed (J. L. GARNETT and S. W. LAW, *Anal. Chim. Acta*, in press).

H. Enz (Switzerland): I would like to ask a rather general question, namely, whether any of the participants know of attempts to do assay work with gas counters in the proportional region instead of the Geiger region. It seems to me that such a procedure could be useful for applications where the activity to be measured was high. I have had occasion myself to make a preliminary attempt. It seems to me that it should be feasible with mixtures of suitable gases.

J. Sharpe (United Kingdom): I know that acetylene has been used in the proportional region. I think the big problem with a great many of the gas-counting methods is that a proportional counter is probably much more sensitive to impurities than a Geiger counter used under the correct conditions.

A. Bainbridge (New Zealand): Acetylene has been used in many laboratories for the routine assay of carbon-14 in work in the proportional region. It is very satisfactory. In fact, all hydrocarbons — e. g. methane, ethane, ethylene — work very well in the proportional region. They are excellent gases for that purpose.

F. Hasan (Finland): I do not think it can be decided one way or the other whether proportional counting is more advantageous than Geiger counting. The former certainly allows for the assay of more active samples, without needing corrections for counter dead time. As regards the impurities in the counting gas, two schools of thought are represented in the literature: that which considers Geiger counting to be more advantageous because more impurities are tolerated in the counting gas, and that which argues that proportional counting is definitely more compatible with impure filling gas. The opinions seem to depend mainly on which is the author's own preferred method. My own experience, based on gas counting and also on gas-flow windowless counting on paper chromatograms, indicates that proportional counting, at least with methane at atmospheric pressure, is more sensitive to contamination with air than, say, Geiger counting with butane at 12 cm Hg pressure or with Q-gas at atmospheric pressure.

A. R. Crathorn (United Kingdom): Having used acetylene in the proportional region for counting carbon-14 and butane in the Geiger region for the measurement of tritium, I would say that in neither case is additional purification necessary.

END OF VOL. I