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Results of the Analysis of the Intercomparison Samples
of the Depleted Uranium Dioxide SR-10

by

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Depleted Uranium Dioxide SR-10

Summary

Samples of a homogeneous powder of depleted uranium dioxide, SR-10, were distributed to 27 laboratories (ANNEX 1) in February 1979 for intercomparison of the precisions and accuracies of wet chemical assay. 7 laboratories reported their results (ANNEX 1). 6 laboratories applied titration procedures, 4 of them applied methods derived from the Davies and Gray procedure (1), and one laboratory used controlled potential coulometry.

An analysis of variance yields for each laboratory the estimates of the measurement errors, the dissolution or treatment errors and the random calibration errors.

The measurement errors vary between 0.01% and 0.10% relative. The differences to the reference value vary between - 0.48% and + 0.87% uranium, but 5 laboratories agree within $\pm 0.25\%$ U with the reference value. The biases of 5 laboratories are greater than expected from their random errors. The mean bias of the 7 laboratories is equal to + 0.03% U. The standard deviation of the laboratory biases is equal to 0.43% U.

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Report

1. Purpose of the Intercomparison

The intercomparison sample of depleted uranium dioxide powder, SR-10, was distributed to 27 laboratories in February 1979. The purpose was to offer to laboratories, dealing with uranium analysis, an opportunity to check the precision and accuracy of their uranium assay measurements.

The application of wet chemical procedures for the determination of uranium with relative precision of the order of 0.1% was recommended.

2. Preparation and Distribution of the Samples

The source material was a batch of depleted uranium dioxide powder of a chemical purity required in the fabrication of sintered pellets of uranium. At the time of the distribution the material was still rather reactive to atmospheric oxygen and moisture (2). Special attention had to be paid to the procedure for controlling the sample stability and correcting for possible changes in the sample composition between distribution and analysis.

2 kg of the source material were homogenized for 2 hours with a Prolabo mixer (model Turbula). 50 tared glass vials with metal screw-caps (Figure 1) received then each about 10 g of the homogenized powder. The sample bottles were tightly capped immediately after filling and their gross-weights were measured with a precision and accuracy of 1 mg.

Each participant received one sample bottle and one empty bottle for a control of the stability of the tare. The participants were asked to report the results of the weighings of the sample bottle and of the control bottle, the analytical results of the measurements of the uranium concentration and the results of the calibration measurements. Report forms were attached to the letter of instructions addressed with the samples to each participant.

3. Characterisation of the Source Material

Immediately after filling of the 50 sample bottles with 10 g fractions of the uranium dioxide, 4 of these bottles were selected randomly and their contents were submitted to an analysis of the uranium concentration and isotopic composition at the Safeguards Analytical Laboratory (SAL) of the IAEA.

The method for chemical assay was the Davies and Gray Potentiometric Titration (1) in the modification recommended by NBL (3) and applied routinely in SAL (4). The measurement system was calibrated with respect to the NBS Standard Reference Material 960 (uranium metal).

The results of these characterisation measurements were submitted to a statistical evaluation. The goal of this evaluation was:

- to verify the homogeneity of the material within and between the sample bottles
- to establish a best estimate of the true uranium concentration as the reference value

- to calculate confidence limits of this reference value, considering the various sources of error.

The atomic weight of the SR-10 material was determined from its isotopic analysis.

The results of the characterisation and their statistical analysis are summarized in Table 1.

The overall mean was adopted as the best estimate of the true concentration.

Reference Value	87.125% U
95% Confidence Limits	\pm 0.026% U
Atomic Weight	238.04

STANDARD
REFERENCE
SERIAL
NO.

UO₂

3 960

3 960

08

03

3 950 a

Table 1 Result of Characterisation Analysis

No. of Measurements: 36
 No. of Dissolutions: 12
 No. of Samples : 4

Source of Variation		Estimate of Std. Dev. (% U)	Degrees of Freedom
Measurement Error	(SI)	0.024	24
Dissolution (Treatment) Error	(SB)	0.013	8
Heterogeneity (Sample) Error	(SA)	0.007	3
Random Calibration Error	(SC)	0.037	9
Certification of NBS-960	(SS)	0.010	19

Mean of 36 Measurements: 87.125% U
 Standard Error* 0.0081 (df = 3)
 95% Confidence Limits ± 0.026% U

Reference Value: 87.125 ± 0.026% U

$$* SE^2 = \frac{SI^2}{36} + \frac{SB^2}{12} + \frac{SA^2}{4} + \frac{SC^2}{10} + \frac{SS^2}{20}$$

Table 1 (continued)

Isotopic composition of SR-10 determined by thermal ionisation
mass-spectrometry

ISOTOP	Atom %	Weight %
234	0.0011	0.0010
235	0.2045	0.2019
236	0.0021	0.0020
238	99.7924	99.7950

Atomic Weight = 238.04

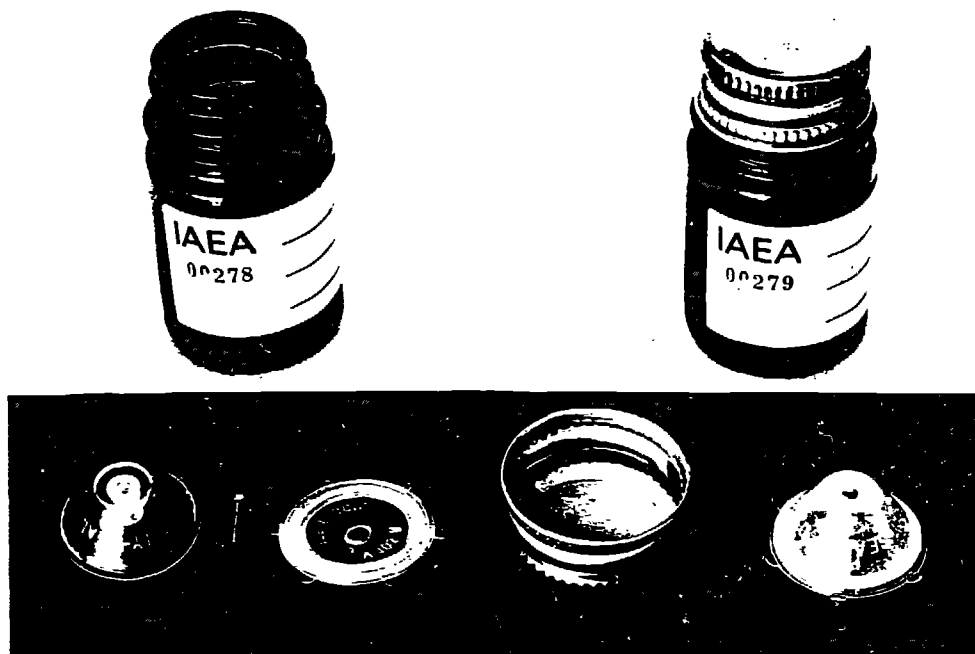


FIGURE 1: Glass Vials with Metal Screw Caps

4. Analysis by the Participating Laboratories

The participants were asked to perform their measurements following the analytical scheme described in Figure 2. The use of wet chemical analytical methods capable to achieve a precision of the order of 0.1% was recommended.

As the material was known to be still rather reactive, the participants were asked to weigh the sample bottles and the empty control bottles prior to analysis, before and after opening of the bottles, and with a precision and accuracy of 1 mg. This method is used successfully to control the sample stability and to correct for changes in the sample composition (2).

The participants were also asked to report the results of their calibration measurements to estimate at least the random calibration error.

All reporting laboratories followed these recommendations.

5. Method of Evaluation of the Results of a Single Laboratory

5.1. Weight Change Corrections

The measurements of the gross-weights of the sample and of the empty control bottle prior to the analysis were used to correct the results for possible moisture pick up and oxidation of the material between the time of distribution and analysis according to equation 1:

$$U_R = U_v \times \frac{(R_a - R_b) + (G_b - T)}{G_a - T} \quad (1)$$

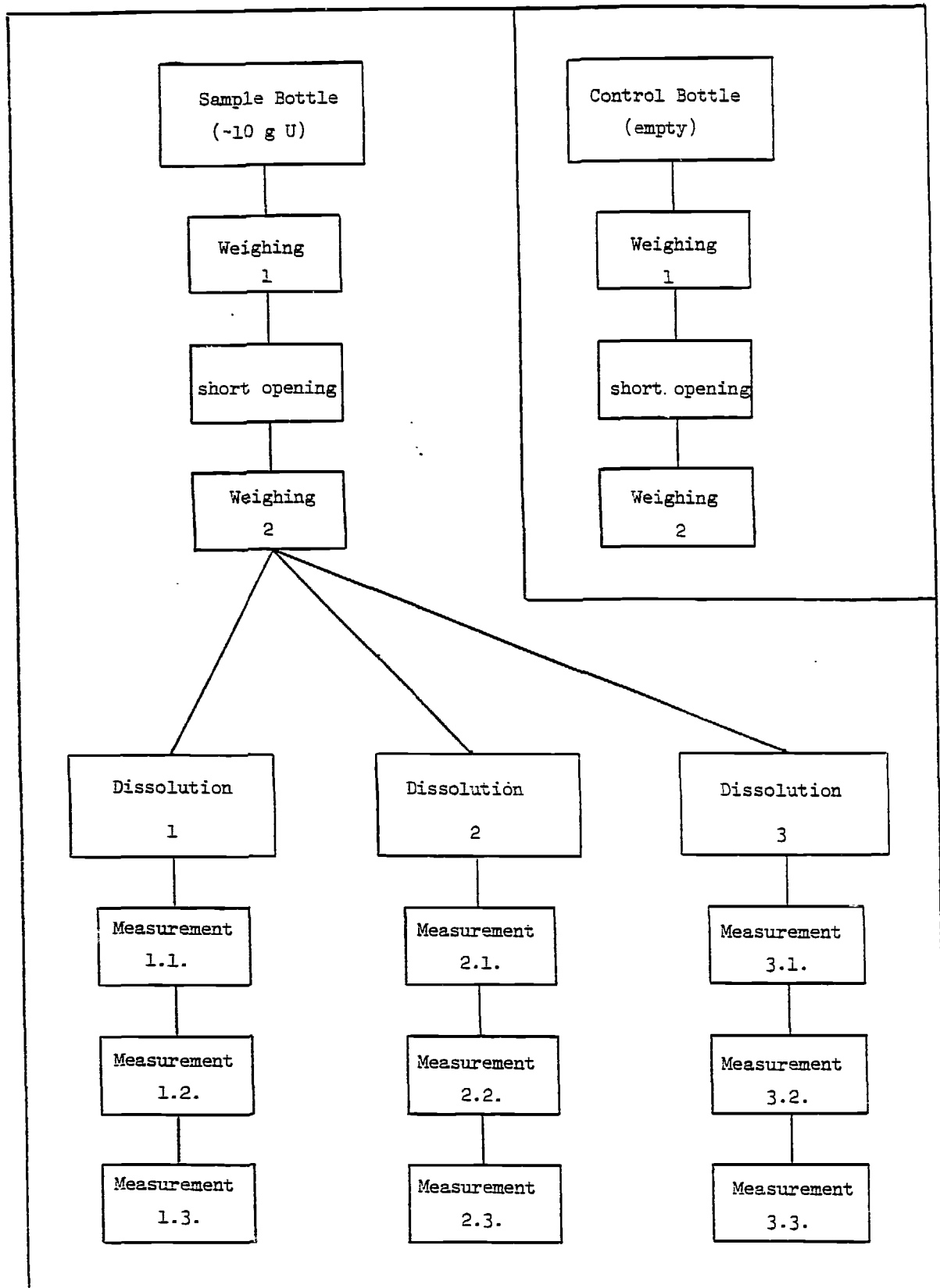


FIGURE 2: Measurement Scheme for a Single Laboratory

where U_v is an individual result of the measurement of the uranium concentration.

R_a and R_b are the weights of the empty control bottle measured at the time of distribution (a) and analysis (b).

G_a and G_b are the gross-weights of the sample bottle at the time of distribution (a) and analysis (b).

T is the tare-weight of the sample bottle.

Previous tests (2) indicated that, when the sample bottles remain perfectly tight, reactive uranium dioxide may absorb the oxygen enclosed in the bottle. This effect may result in a 0.06% decrease of the uranium concentration. The participants were therefore asked to repeat weighings of the sample bottles after a brief opening in order to estimate the magnitude of this effect in the present experiment and to correct for it.

5.2. Outline of the Evaluation of the Analytical Results of a Single Laboratory

The results of each laboratory corrected for weight changes were submitted to a one-way variance analysis as described in ANNEX 2. This statistical analysis yields estimates for the measurement and the treatment or dissolution errors. It also tests the statistical significance of the variability between replicate dissolutions, when compared to the estimate of the measurement error. The standard error, SE, of the mean of the

analytical results is a measure of the combined contributions of the measurement and treatment random errors of the laboratory.

The standard error of the calibration, SEC, was calculated from the number, n_c , and the standard deviation, SC, of the calibration measurements

$$SEC = \frac{SC}{\sqrt{n_c}} \quad (df_c = n_c - 1) \quad (2)$$

This parameter measures only the contribution of the random errors in the calibration.

The standard error of the results, SE, and the standard error of the calibration, SEC, were combined to estimate the total standard error, SET, of the laboratory mean:

$$SET^2 = SE^2 + SEC^2 \quad (df = 2) \quad (3)$$

The 95% confidence limits of this mean result were calculated by

$$C.L.(95\%) = \pm SET \times 4.303 \quad (4)$$

where 4.303 is the value of Student's factor t (5) for 2 degrees of freedom and 95% probability level.

Finally the mean result of a laboratory was compared to the reference value (87.125% U)

$$\text{BIAS} = \bar{X}_{QQ} - 87.125 \quad (5)$$

where \bar{X}_{QQ} is the mean result of the laboratory.

The Null-Hypothesis (BIAS = 0) was tested by a t-test:

$$\hat{t} = \frac{|\text{BIAS}|}{\sqrt{\text{SET}^2 + 0.0081^2}} \quad (6)$$

(0.0081 is the standard error of the reference value).

\hat{t} was compared with the Student's t-table (5):

$$t(95\%;2) = 4.303$$

The result of the comparison is expressed by one of the following statements:

Statistically not significant, if $\hat{t} < t(95\%;2)$

Statistically significant, if $\hat{t} \geq t(95\%;2)$

Note that this test considers only the random errors. The detection of a "significant" bias indicates therefore that the systematic errors of the mean result are probably equal to or larger than the random errors.

The statistical evaluation assumed also that the random errors were independent and normally distributed. If these assumptions are not correct the evaluation may underestimate the combined contribution of these errors.

5.3. Evaluation Sheet

Each participant received an Evaluation Sheet (Figure 3) presenting in two successive pages the results of the evaluation of its own results. The Evaluation Sheet provides:

- the laboratory code (1)
- the results of the weight measurements of the sample and of the empty control bottle (2)
- the results of the evaluation of the analytical results of the laboratory (3) consisting of:
 - a short explanation of the results concerning the precision of the analytical method as applied by that laboratory (3.1.)
 - a brief discussion of the accuracy of the analytical results (3.2.), and
 - a table of results (3.3.) including the results of the 9 individual measurements corrected for weight changes,

the dissolution means and standard deviations, the overall mean, \bar{X} , the estimates of the standard deviations of the measurement (SI) and treatment error (SH), the standard error of the results (SE) and of the calibration (SEC), the combined standard error (SET), the 95% confidence limits of the overall mean (C.L.) and the difference to the reference value (BIAS). Finally the results of three statistical tests are reported:

a) a Student's t-test to judge of the significance of the laboratory bias, when compared to the random errors

b) a Bartlett χ^2 -test to judge of the consistency of the measurement precisions on the three replicate dissolutions, and

c) a Snedecor F-test to judge of the significance of the variability between dissolution means, when compared with the measurement error.

IAEA ANALYTICAL QUALITY CONTROL SERVICE
INTERNATIONAL ATOMIC ENERGY AGENCY

EVALUATION SHEET FOR SR-10

1. YOUR LABORATORY CODE IS (X) (ABC) ()

2. RESULTS OF WEIGHT CORRECTION :

WEIGHT CHANGE OF SAMPLE BOTTLE	IAEA 303	0.003 103
WEIGHT CHANGE OF CONTROL BOTTLE	IAEA 373	0.005 103
NET WEIGHT CHANGE		0.008 103
NET WEIGHT OF SAMPLE (13-FEB-79)		10.273 103
RELATIVE NET WEIGHT CHANGE		0.003 121
CORRECTION FACTOR APPLIED		1.00083

3. ANALYTICAL RESULTS :

3.1. PRECISION :

YOUR RESULTS HAVE BEEN EVALUATED TO ESTIMATE THE MAGNITUDE OF THREE POSSIBLE ERROR COMPONENTS. THE EVALUATION YIELDS THE FOLLOWING ESTIMATES OF STANDARD DEVIATIONS :

MEASUREMENT	0.064	DF = 6	N = 9
TREATMENT	0.155	DF = 2	N = 3
CALIBRATION	0.054	DF = 0	N = 9

THE STANDARD ERROR OF YOUR MEAN RESULT, ESTIMATED BY A PROPAGATION OF THE ABOVE ERROR COMPONENTS, IS EQUAL TO 0.094 % U. CONSEQUENTLY WITH 2 DEGREES OF FREEDOM THE 95 % CONFIDENCE LIMITS OF YOUR MEAN ARE EQUAL TO ± 0.403 % U.

FIGURE 3: Evaluation Sheet (2 pages)

3.2. ACCURACY :

THE REFERENCE VALUE OF THE SR-10 MATERIAL IS EQUAL TO 07.125 % U WITH A STANDARD ERROR OF 0.001 % U (DC = 3). THE OVERALL MEAN OF YOUR RESULTS IS 06.641 % U AND DIFFERS BY -0.404 % U FROM THE REFERENCE VALUE. THIS DIFFERENCE IS STATISTICALLY SIGNIFICANT AT THE 95.0 % PROBABILITY LEVEL. THIS JUDGEMENT IS BASED ON A T TEST OF THE NULL HYPOTHESIS AND TAKES INTO ACCOUNT THE ABOVE ESTIMATES OF THE STANDARD ERRORS OF YOUR RESULT AND OF THE REFERENCE VALUE.

3.3. TABLE OF RESULTS :

1% U CORR'D	DISSOLUTION 1	DISSOLUTION 2	DISSOLUTION 3
ALiquot 1	06.732	06.502	06.722
ALiquot 2	06.692	06.522	06.702
ALiquot 3	06.622	06.371	06.022
MEAN	06.602	06.465	06.775
STD. DEV.	0.056	0.082	0.050

RESULT OF ONE-WAY VARIANCE ANALYSIS			
SYMBOL	VALUE	DF	EXPLANATION
X00	06.641		OVERALL MEAN
ST	0.149	8	TOTAL STANDARD DEVIATION
SI	0.064	6	MEASUREMENT ERROR
SH	0.155	2	TREATMENT ERROR
SE	0.092	2	STANDARD ERROR OF RESULTS
SEC	0.010	0	STANDARD ERROR OF CALIBRATION
SEI	0.094	2	COMBINED STANDARD ERROR
C.L.	0.403		95 % CONFIDENCE LIMITS OF MEAN
XR	07.125		REFERENCE VALUE
SER	0.001	3	STANDARD ERROR OF REFERENCE VALUE
BIAS	-0.404		DEVIATION FROM REFERENCE VALUE
T	5.155	2	T-TEST ON SIGNIFICANCE OF BIAS
SLT	>95.0 %		PROBABILITY LEVEL OF T-VALUE
CHI200	0.445	6	BARTLETT TEST ON HOMOGENEITY OF GROUP
SLC	19.9 %		VARIANCES AND PROBABILITY LEVEL
F	10.557	12/6	F-TEST ON SIGNIFICANCE OF TREATMENT
SLF	99.7 %		ERROR AND PROBABILITY LEVEL

6. Results of the Individual Laboratories

6.1. Results of the Weight Change Corrections

The results of the measurements of the bottle weights are summarized in Table 2. The net weight changes of the sample bottles vary between 0.06% and 0.35% relative to the net weights of the samples. No bottle appeared as "perfectly tight" and therefore the weight changes which were measured on the bottles as received were used for correction of the uranium concentration results rather than the weight changes measured after a short opening of the bottles.

Table 2 Bottle Weight Changes

Lab.No.	1 Weight Change Sample (G)	2 Weight Change Contr. (G)	3 NET Weight Change 3 = 1 - 2	Relative Weight Change (%)
3	0.003	- 0.005	0.008	0.083
6	0.038	0.000	0.038	0.354
8	0.006	0.000	0.006	0.059
20	0.017	0.000	0.017	0.153
22	0.009	- 0.002	0.011	0.105
25	0.004	- 0.002	0.006	0.057
28	0.012	- 0.003	0.015	0.130
N	7	7	7	7
\bar{x}	0.013	- 0.002	0.015	0.134
	0.012	0.002	0.011	0.103

According to these data the mean change in the composition of the material between the time of its distribution and its analysis is 0.13%, which indicates a rather high reactivity of the material.

6.2. Results of the Uranium Concentration Measurements

The outcome of the statistical treatments on the results of the individual laboratories is summarized in Table 3.

The data demonstrate that the precisions of the 7 reporting laboratories are very good. The standard deviations of their measurements vary between 0.01 and 0.09% U. The standard deviations for the treatment errors vary between zero (negative variance component, see ANNEX 2) and 0.15% U. In three cases the variability between replicate dissolutions is significant at the 99% probability level, when compared to the measurement error by means of Snedecor F-Tests.

The mean results of most laboratories (actually 5) differ more from the reference value than would be expected if the errors were only random. As we stated in Section 5.2., this indicates that in most cases the systematic errors, not included in the evaluation, are effectively large compared to the random errors.

Table 3 Analytical Results of Participating Laboratories

LAB. NUMBER	LAB. MEAN	LAB. BIAS	MEASURE- MENT ERROR (SI)	TREAT- MENT ERROR (SH)	CALIBRA- TION ERROR (SC)	No. OF CALIB. MEASURE- MENTS	COMBINED STANDARD ERROR (SET)	95% CONF. LIMITS OF LAB. MEAN (%U)	SIGNIFIC- ANCE OF LAB. BIAS /% PROBA- BILITY ⁷ (RESULT OF t-TEST)	SIGNIFIC- ANCE OF TREATMENT ERROR /% PROBA- BILITY ⁷ (RESULT OF F-TEST)	ANALYTICAL METHOD APPLIED	STANDARD REFERENCE MATERIAL USED
3	86.64	- 0.48	0.064	0.155	0.054	NOT REP. 9 ASSUMED	0.094	0.40	> 95%	99.7	NBL D + G	SALE UO ₂
6	88.00	+ 0.87	0.090	SH ² <0	0.015	3	0.018	0.08	> 99.9%		D + G; visual endp.	UO ₂
8	86.99	- 0.13	0.011	0.024	0.011	4	0.016	0.07	> 95%	99.6	NBL D + G	NBS 960
20	87.30	0.17	0.017	0.031	0.017	3	0.021	0.09	> 95%	99.1	NBL D + G	NBS 960
22	87.12	- 0.01	0.073	SH ² <0	0.087	9	0.031	0.13	< 95%		CP COULOMETRY	U ₃ O ₈
25	87.14	+ 0.01	0.051	SH ² <0	0.078	10	0.029	0.13	< 95%		Ti(III)-REDUCT- ION; CEROMETRY	AS ₂ O ₃
28	86.88	- 0.25	0.060	SH ² <0	0.124	9	0.043	0.19	> 95%		①	NBS 950 a

① Purification by reversed-phase chromatography; reduction by Jones-Reductor; oxidimetric titration with Cr(VI) to visual endpoint

Systematic errors may be due to:

- a. Calibration errors in the standardization of the analytical procedure, including uncertainties in the composition assigned to the reference material
- b. Weighing errors in the analytical procedure and the weight change correction
- c. Systematic errors of the characterization analysis.

The magnitude of the deviations of laboratories 3 and 6 would deserve a more detailed examination.

7. Interlaboratory comparisons

7.1. Fluctuations between Laboratories

The analytical results of the 7 reporting laboratories were submitted to a two-way variance analysis. This statistical evaluation yields estimates of the standard deviation components for the mean measurement error (SIQ), the mean treatment error (SB) and the between laboratories fluctuation (SA). It also tests the statistical significance of the mean treatment error and the between laboratories variability by means of Snedecor F-Tests. Bartlett's χ^2 -tests allow to judge of the consistency of the measurement and treatment errors. The outcome of this statistical analysis is presented in Table 4. The random calibration errors need not to be considered in this evaluation, as the random as well as the systematic calibration errors influence directly the laboratory means and are therefore contained in the between laboratory variability.

The data show that the measurement errors as well as the treatment errors of the individual laboratories cannot be considered equal. This result is not surprising, and reflects the fact that the laboratories used different analytical procedures and measurement conditions.

The standard deviation of the laboratory biases

$$SA = 0.427\% U \quad (df = 6)$$

is too large to be due only to the random calibration errors. The mean standard error of the calibration measurement is indeed only

$$\overline{SEC}^2 = \frac{\sum_{i=1}^7 SEC_i^2 (n_{c_i} - 1)}{\sum_{i=1}^7 n_{c_i} - 7} \quad (7)$$

$$\overline{SEC} = 0.028\% U \quad (df = 34)$$

A Snedecor F-test evidently indicates that SA is significantly higher than \overline{SEC} .

This of course confirms the conclusions of the evaluation of the results of individual laboratories (Section 6.2.): the laboratory biases are essentially due to systematic errors which remain to be identified.

Table 4 Two-Way Variance Evaluation of the Results of
all participating Laboratories

MEAN MEASUREMENT ERROR, SIQ:	0.059% U (df = 42)
PROBABILITY LEVEL OF χ^2 :	98% PROBABILITY
(→ VARIANCES NOT CONSISTENT)	
MEAN TREATMENT ERROR, SB:	0.055% U (df = 14)
PROBABILITY LEVEL OF χ^2 :	99% PROBABILITY
(→ VARIANCES NOT CONSISTENT)	
PROBABILITY LEVEL OF F:	99.9% PROBABILITY (df = 14/42)
(→ TREATMENT ERROR HIGHLY SIGNIFICANT)	
BETWEEN LABORATORIES ERROR, SA:	0.427% U (df = 6)
PROBABILITY LEVEL OF F:	100% PROBABILITY (df = 6/14)
(→ HIGHLY SIGNIFICANT FLUCTUATION BETWEEN LABORATORIES)	

In fact, looking at the laboratory means in Table 3, laboratory 6 appears as an outlier: a Nalimow outlier test indicates indeed a 99% probability for this assumption. However, if the results of this laboratory are rejected, the conclusions of the statistical evaluation remain unchanged. The results of the two-way variance analysis excluding the results of laboratory 6 are shown in Table 5.

Table 5 Result of Two-way Variance Analysis excluding the Results of Laboratory No. 6.

SIQ	0.052% U
PROB. OF χ^2	96% PROB.
SB	0.062% U
PROB. OF χ^2	99% PROB.
PROB. OF F	100% PROB.
SA	0.226% U
PROB. OF F	99.9% PROB.

7.2. Deviation from the Reference Value

Figure 4 provides a graphical comparison of the mean result of each laboratory with respect to the reference value. According to Table 3, five laboratory means differ significantly from the reference value at the 95% probability level. This is, as we said, quite a high proportion. This test, however, is not a measure of the accuracy of the analysis. It signals rather when the "bias" becomes significantly greater than the random errors. Indeed, the results of three of those laboratories differ only by 0.25% U or less from the reference value. According to current standards, their accuracy is certainly satisfactory, still their biases appear to differ significantly from zero, because the precisions of these 3 laboratories are very high.

The grand mean of all laboratories is equal to

$$\bar{X}_{QQQ} = 87.15\% U \quad (N = 63 \text{ measurements}).$$

The mean bias with respect to the reference value is therefore

$$\bar{d} = + 0.03\% U \quad (N = 63)$$

The standard error of the mean bias can be estimated by:

$$SED^2 = \frac{SA^2}{7} + \frac{SB^2}{21} + \frac{SIQ^2}{63} \quad (8)$$

$$SED = 0.162 \quad (df = 6)$$

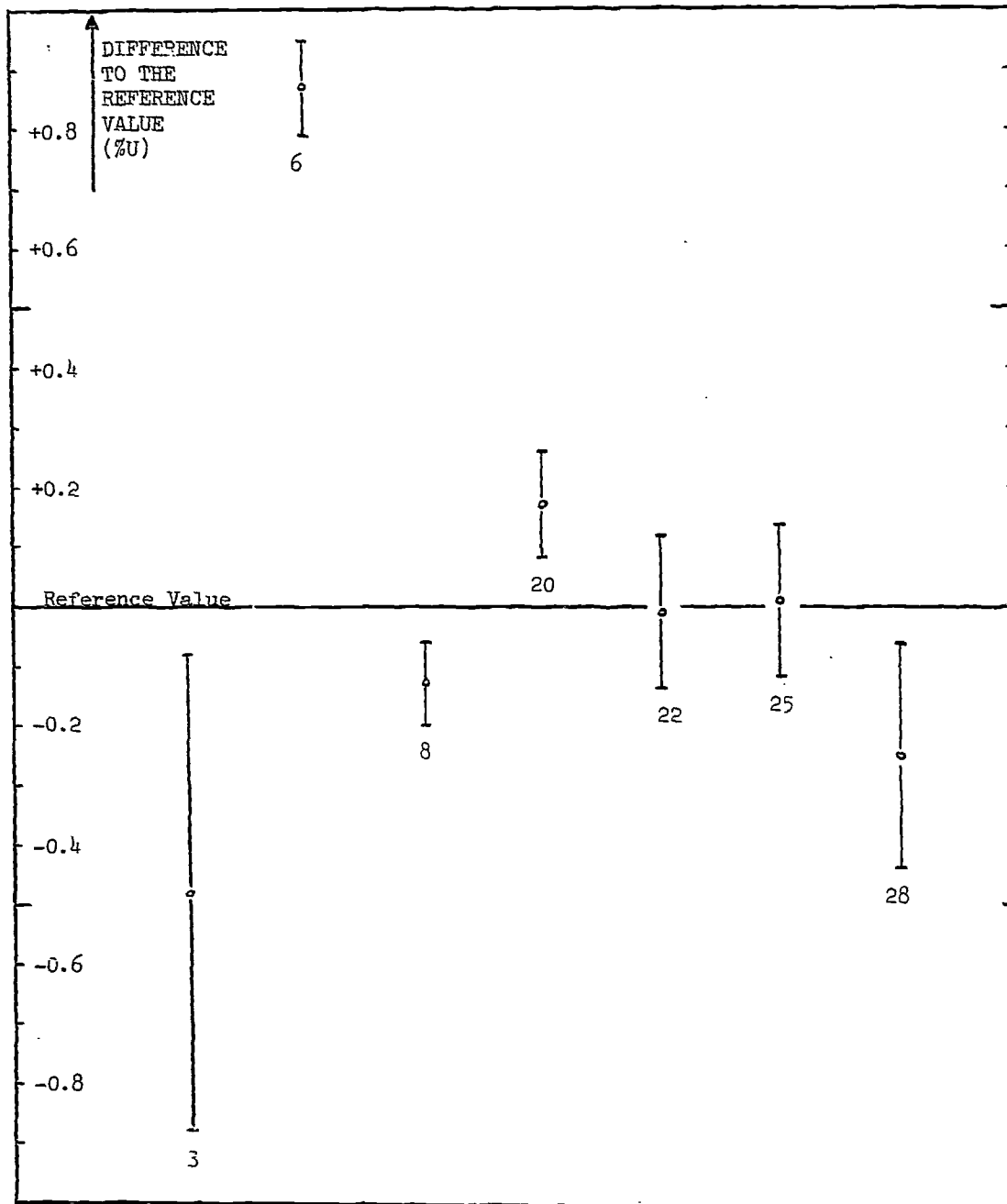


FIGURE 4: Laboratory Means with 95% confidence limits with respect to the Reference Value (87.125 %U)

A Student t-Test

$$t = \frac{\bar{d}}{\sqrt{SED^2 + 0.0081^2}} \quad (9)$$

$$t = 0.2 \quad \sqrt{t(6; 95\%) = 2.457}$$

indicates that the mean bias is not significantly different from zero at a 95% probability level; that means, no difference between the grand mean and the reference value can be detected.

The same statement results, if the results of laboratory 6 are rejected from the evaluation.

$$\bar{d} = -0.12\% \text{ U} \quad (N = 54)$$

$$SED = 0.094 \quad (df = 5)$$

$$t = 1.23 \quad (t(5; 95\%) = 2.57)$$

8. Conclusion

Only a quarter of the interested laboratories submitted the results of their analysis.

All of the 7 reporting laboratories used wet chemical methods. Their results showed an average relative precision of the order of 0.1%. Dissolution errors and random calibration errors were of the same order of magnitude. The mean relative deviation of 0.03% with respect to the reference value is statistically not significant. The coefficient of variation of the laboratory systematic errors is equal to 0.5%; it is the main cause for the spread of the data.

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ANNEX 1

List of Participating Laboratories

1. Nuclear Research Center, Rez, CSSR
2. Enstitüsü Genel Direktörlüğü Eskisehir Yolu Üstü, Ankara, Turkey
3. Institute for Energetic Nuclear Reactors, Colibasi, Romania
4. Eldorado Nuclear Ltd., Port Hope, Ont., Canada
5. Radiation Management Corp., Philadelphia, PA, USA
6. Atomic Energy Organization of Iran, Teheran, Iran
7. British Nuclear Fuels Ltd., Chester, Cheshire, UK
8. Instituto Peruano de Energia Nuclear, Lima, Peru
9. Korea Research Institute of Geoscience and Mineral Resources, Seoul, Korea
10. Korean Atomic Energy Research Institute, Seoul, Korea
11. Bhaba Atomic Research Centre, Bombay, India
12. Savannah River Laboratory, Aiken, S.C., USA
13. National Research Institute for Radiobiology and Radiohygiene, Budafok, Hungary
14. Staatliches Amt für Atomsicherheit und Strahlenschutz, Aussenstelle Lohmen, Lohmen, DDR
15. Lawrence Livermore Laboratory, Livermore, Cal., USA
16. Maden Tetkik ve Arama Enstitüsü, Ankara, Turkey
17. Staatliches Amt für Atomsicherheit und Strahlenschutz der DDR, Berlin, DDR
18. Instituto de Energia Atomica, Sao Paulo, Brazil
19. Comision Nacional de Energia Atomica, Buenos Aires, Argentina
20. National Council for Scientific Research, Lusaka, Zambia

List of Participating Laboratories

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22. University of Helsinki, Helsinki, Finland
23. Atomic Energy Mineral Centre, Lahore, Pakistan
24. Atomic Energy Establishment, Tripoli, Libya
25. Wroclaw Technical University, Wroclaw, Poland
26. Office of Atomic Energy for Peace, Bangkok, Thailand
27. Nuclear Chemistry Division, Nilore, Rawalpindi, Pakistan

ANNEX 2

One-Way Variance Analysis for the Statistical Evaluation of the Results of a Single Laboratory

1. Objectives and Model of the Evaluation

In the present experiment, the results of a given laboratory may be considered to carry three independent sources of fluctuations or errors:

- (i) the systematic error, a , or bias of the laboratory with respect to the reference value, XR
- (ii) the dissolution or treatment error, b
- (iii) the measurement error, c .

The j -th result of dissolution or treatment i may thus be described by the following linear equation

$$x_{ij} = XR + a + b_i + c_{ij} \quad (A-1)$$

We shall assume that the terms b_i and c_{ij} are not only independent but that they are also normally distributed around a zero mean. The data reported by a given laboratory constitute a nested population liable to a one-way variance analysis.

The purpose of this analysis is:

- a) to detect if the treatment errors are statistically significant
- b) to estimate the magnitude of the random errors, c and b , of the laboratory, i.e. their standard deviations SI and SH
- c) to calculate the confidence limits of the laboratory mean
- d) to estimate the bias, a , of the laboratory and test its statistical significance.

2. Indices and Size of Groups

All results obtained on the same dissolution or after a given treatment are said to constitute a group.

L_i is the number of measurements in group i

K is the number of groups

$N = \sum_{i=1}^K L_i$ is the total number of measurements

$j = (1, 2, \dots, L_i)$ identifies the j -th measurement in group i

$i = (1, 2, \dots, K)$ identifies the i -th group.

3. Arithmetic Means

Mean of group i

$$\bar{x}_i = \frac{\sum_{j=1}^{L_i} x_{ij}}{L_i} \quad (\text{A-2})$$

overall mean

$$\bar{x} = \frac{\sum_{i=1}^K \sum_{j=1}^{L_i} x_{ij}}{N} \quad (\text{A-3})$$

4. Variances

4.1. Total variance, ST^2

$$ST^2 = \frac{\sum_{i=1}^K \sum_{j=1}^{L_i} (x_{ij} - \bar{x})^2}{N - 1} \quad (\text{A-4})$$

4.2. Variance of group i, s_i^2

$$s_i^2 = \frac{\sum_{j=1}^{L_i} (x_{ij} - \bar{x}_i)^2}{L_i - 1} \quad (\text{A-5})$$

4.3. Average group variance ("Measurement Error"), SI^2

$$SI^2 = \frac{\sum_{i=1}^K \sum_{j=1}^{L_i} (x_{ij} - \bar{x}_i)^2}{N - K} \quad (A-6)$$

4.4. Between group variance, SZ^2

$$SZ^2 = \frac{\sum_{i=1}^K [(\bar{x}_i - \bar{x})^2 \cdot L_i]}{K - 1} \quad (A-7)$$

5. Variance of the "Treatment Error", SH^2

$$SH^2 = \frac{K - 1}{N - \frac{\sum_{i=1}^K (L_i)^2}{N}} \cdot (SZ^2 - SI^2) \quad (A-8)$$

If SI^2 is larger than SZ^2 a negative variance SH^2 results. In that case SH is assumed to be equal to zero.

This formula simplifies if the nested network is balanced, i.e. that all groups have equal size L' . Then:

$$SH^2 = \frac{1}{L'} \cdot (SZ^2 - SI^2) \quad (A-9)$$

6. Standard Error, SE

$$SE^2 = \frac{SI^2}{N} + \frac{SH^2}{\frac{K}{\sum_{i=1}^K L_i^2}} \quad (A-10)$$

If the scheme is balanced, this formula simplifies to:

$$SE^2 = \frac{SI^2}{N} + \frac{SH^2}{K} \quad (A-11)$$

This standard error expresses the uncertainty on the laboratory mean due to the propagation of the random errors only.

7. Degrees of Freedoms

VARIANCE	DEGREES OF FREEDOM
ST^2	DF = N - 1
SI^2	DFI = N - K
SZ^2, SH^2, SE^2	DFZ = K - 1

8. Bartlett Test

This is a test of the consistency of the variances s_i^2 with respective degrees of freedom $f_i = L_i - 1$.

$$\text{Let } f_I = \sum_{i=1}^K f_i \quad (\text{A-12})$$

$$\text{and } \alpha_I = \frac{\sum_{i=1}^K \frac{1}{f_i} - \frac{1}{f_I}}{3(K-1)} + 1 \quad (\text{A-13})$$

$$\text{then } PB = \frac{1}{\alpha_I} \cdot (f_I \cdot \ln SI^2 - \sum_{i=1}^K f_i \cdot \ln s_i^2) \quad (\text{A-14})$$

Compare the calculated value of PB with the value of the χ^2 -function for $K - 1$ degrees of freedom. This test results in one of the following statements:

"no differences detectable", if	$PB < \chi^2(95)$
"differences are probable", if	$\chi^2(95) \leq PB < \chi^2(99)$
"differences are significant", if	$\chi^2(99) \leq PB < \chi^2(99.9)$
"differences are highly significant", if	$\chi^2(99.9) \leq PB$

Instead of comparing PB with the table-values for the respective probability levels, a series approximation allows to compute the Significance Level of PB.

9. Snedecor Test

This is a test of the significance of the variability between groups or treatments.

$$\text{Calculate } \hat{F} = \frac{SZ^2}{SI^2} \quad (A-15)$$

and compare with the Snedecor table for $\nu_1 = K - 1$ and $\nu_2 = N - K$ degrees of freedom.

The Level of Significance can be again calculated by using a series approximation.

The result of the test is expressed by one of the following four statements:

"no difference between SZ and SI detectable", if $\hat{F} < F(95)$

"SZ is probably higher than SI", if $F(95) \leq \hat{F} < F(99)$

"SZ is significantly higher than SI", if $F(99) \leq \hat{F} < F(99.9)$

"SZ is highly significant higher than SI", if $F(99.9) \leq \hat{F}$

