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**TRITIUM RELEASE FROM LITHIUM CERAMICS AT CONSTANT  
TEMPERATURE: ANALYSIS METHODS**

**LIBÉRATION DE TRITIUM PAR LES CÉRAMIQUES AU  
LITHIUM À TEMPÉRATURE CONSTANTE:  
MÉTHODE D'ANALYSE**

**R.A. VERRALL and J.M. MILLER**

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February 1992 février

AECL Research

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RÉSUMÉ

Dans le présent rapport, on examine les méthodes d'analyse que l'on utilise dans les essais de recuit, après irradiation, pour mesurer les quantités de tritium libérées par les céramiques au lithium à une température constante. On y décrit les modifications apportées aux relations de Bertone (1) dans le but de différencier le processus de libération régi par diffusion et le processus de libération régi par désorption. Les méthodes sont appliquées à des essais effectués sur du  $\text{LiAlO}_2$  fritté. On démontre qu'un processus de désorption du premier ordre régit la libération du tritium dans ces essais.

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ABSTRACT

Analytic methods for post-irradiation annealing tests to measure tritium release from lithium ceramics at constant temperature are examined. Modifications to the Bertone (1) relations for distinguishing diffusion-controlled release from desorption-controlled release are shown. The methods are applied to tests on sintered  $\text{LiAlO}_2$ ; first-order desorption is shown to control tritium release for these tests.

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## 1. INTRODUCTION

Out-reactor tritium-release tests on lithium ceramics are being used to determine the kinetics of tritium release and to understand the processes involved (e.g., 1-5). These, and in-reactor tests, provide the information needed to model tritium release and retained inventory in an ITER-type blanket. Understanding the factors that control release also helps to find ways to minimize tritium inventory. Invalid assumptions about the mechanism(s) that control release in the experimental tests can lead to incorrect results. Bertone (1) provided a number of criteria to be applied to release data to help distinguish whether diffusion in the bulk or desorption from the surface (or both) are rate-controlling. In this report, the basic methods of analysis are reviewed, the tests of Bertone modified for use in practical situations with finite-volume ionization chambers or proportional counters, and the methods applied to data on  $\text{LiAlO}_2$ .

## 2. METHODS OF ANALYSIS

When tritium release from a sphere of radius  $a$  is controlled by diffusion, simple application (6) of Fick's first law of diffusion provides the following release formula:

$$f = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 D \pi^2 t / a^2) \quad (1)$$

where  $f$  is the fractional tritium release at time  $t$  (i.e., the release at time  $t$ , normalized by the total release), and  $D$  is the diffusion coefficient at temperature  $T$ .

Approximations (7,8) of this formula suffice for certain applications:

$$f = 6 \left( \frac{Dt}{\pi a^2} \right)^{1/2} \quad \text{for } f \leq 0.3 \quad (2)$$

$$f = 6 \left( \frac{Dt}{\pi a^2} \right)^{1/2} - \frac{3D}{a^2} t \quad \text{for } f \leq 0.95 \quad (3)$$

When release is controlled by desorption from the surface, the following differential equation applies (9):

$$\frac{d}{dt} c(t) = -kc(t)^n$$

where  $c(t)$  is the concentration in the sample,  $k$  is the desorption coefficient, and  $n$  is the order of desorption. Note that since diffusion is rapid compared to desorption, the tritium concentration will remain relatively uniform throughout the specimen; i.e.,  $c(t)$  is not a function of position.

The above equation represents the definition of  $n^{\text{th}}$  order desorption, and  $k$  is assumed to be constant. For first- and second-order desorption, the differential equation can be integrated, with the following results:

$$\text{first order} \quad f = 1 - e^{-kt} \quad (4)$$

$$\text{second order} \quad f = \frac{kt}{1 + kt} \quad (5)$$

It is possible to include various geometric and material factors (such as sphere diameter) in the definition for  $k$ . For example, for spheres, a factor 3 is usually included in the first-order exponential (see Ref. 1 for its origin).

Bertone (1) showed that, for both diffusion- and desorption-controlled release,  $f$  must satisfy the following:

$$\frac{d^2 \ln(f)}{d \ln(t)^2} < 0 \quad (6)$$

Therefore, this equation represents a first check on the consistency of the measurements of a constant temperature, out-reactor release test ( $f$  need not be normalized in this equation because the derivative is unaffected by multiplying  $f$  by a constant factor).

Bertone also showed that the following formula must apply for diffusion-controlled release:

$$\lim_{t \rightarrow 0} \frac{d \ln(f)}{d \ln(t)} = \frac{1}{2} \quad (7)$$

and for desorption-controlled release:

$$\lim_{t \rightarrow 0} \frac{d \ln(f)}{d \ln(t)} = 1 \quad (8)$$

These equations are simply derived from equation 2 for diffusion and equations 4 and 5 for first- and second-order desorption. Bertone showed that they have wide applicability; e.g., for mixes of sizes and shapes of the ceramic particles and for various irradiation conditions. He also said that, for diffusion-controlled release, the sample must be heated very rapidly, and that in all cases, a new zero for time must be taken at approximately the tritium-release peak maximum.

If the release tests can be shown to satisfy equations 6, 7 or 8, then the next step is to obtain  $D$  (or  $k$ ) by fitting the data to equation 1 (or 4 or 5). Good fits to one of these formulas would show that release had been controlled by diffusion (or first-order or second-order desorption) throughout the test, and give confidence to the value of  $D$  (or  $k$ ) so obtained.

The quantity actually measured by the ionization chamber (or proportional counter) in post-irradiation release tests is not the fractional release  $f(t)$ , but the tritium recovery rate,  $r(t)$ ; i.e., the quantity of tritium per unit time. The recovery rate is the time derivative of the fractional release, multiplied by the total tritium recovered. Thus, the recovery rates are the derivatives of equations 1, 4 and 5:

diffusion: 
$$r(t) = 6A\left(\frac{D}{\pi a^2 t}\right)^{3/2} - 3\frac{AD}{a^2} \quad (9)$$

first-order desorption: 
$$r(t) = Ake^{-kt} \quad (10)$$

second-order desorption: 
$$r(t) = \frac{Ak}{(1 + kt)^2} \quad (11)$$

where A is the total recovered tritium in each case. Note that equation 3 was used for diffusion, rather than equation 1, for simplicity, and that the result, equation 9, may be applicable over a smaller region than equation 3 because of the differentiation. These formulas, rather than the formulas for  $f$ , can then be used directly for fitting the ion chamber measurements. Both A and D (or k) can be varied in the fitting routine, or just D (or k), determining A, the total tritium release, from the measurements.

### 3. MODIFICATIONS IN THE USE OF BERTONE'S FORMULAS

In practise, the recovery rate of tritium will never follow the diffusion-controlled relation, equation 9, at small times, even when the release of tritium is controlled by diffusion. This is because the formula diverges (goes to infinity) at  $t=0$ , showing that the formula cannot be meaningful at  $t=0$ . Ionization chambers and proportional counters, used for measuring tritium, have an internal volume that contains the tritium that is being measured. As the tritium enters the chamber, the tritium concentration in the chamber increases from zero to a finite maximum, and then decreases. Since the recovery rate does not follow equation 9 at small times (in particular, since it does not behave like  $t^{-3/2}$ ), it can be shown that

$$\lim_{t \rightarrow 0} \frac{d \ln(f)}{d \ln(t)} \neq \frac{1}{2}$$

contrary to the predictions of equation 7. Surprisingly, no matter what the shape of the tritium release curve, and no matter what point along the curve is selected as  $t=0$  (e.g., the peak maximum), the above limit is equal to 1. (See Appendix 1 for a simple proof.)

Although this limit is 1 for all tritium release curves, diffusion and desorption control can still be distinguished by examining  $\ln(f)/\ln(t)$ , not in the limit as  $t$  goes to 0, but for longer times; i.e., many times the instrument time constant. To demonstrate this, computer simulations of diffusion- and desorption-controlled tritium release have been performed, including convoluting the theoretical release rates with an ion-chamber response function. Figure 1 shows a typical ion-chamber (or proportional counter) response to a sudden injection of tritium at  $t=0$ , followed by no further tritium input. If the chamber volume is  $V$  and gas flow rate is  $F$ , then the response decreases exponentially with a time constant  $V/F$ ; i.e.,  $e^{-(F/V)t}$ . Then, the ion-chamber response to a general tritium input is mathematically obtained by convoluting the input with this response function.

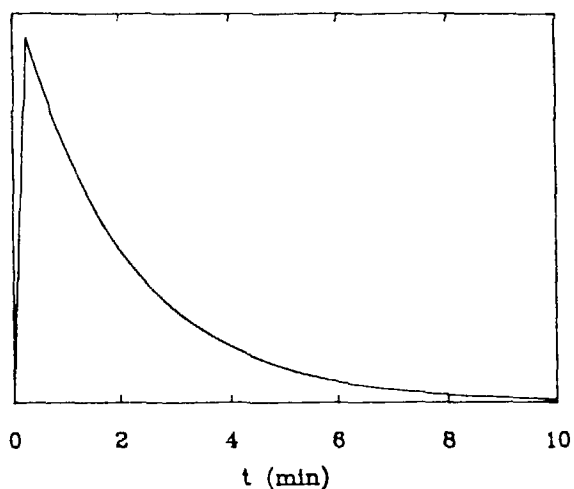


Fig. 1 Ion-chamber response to a sudden injection of tritium at  $t=0$ , followed by no further tritium input. This computer-calculated response is typical for the response of ion chambers or proportional counters, exponentially decreasing from a peak maximum. The cusp at the maximum is an artefact due to computer techniques. The vertical axis is tritium concentration or tritium recovery rate in arbitrary units.

To model diffusion-controlled release, artificial data were generated using equation 9. This data set was then convoluted with the ion-chamber response curve to generate the "measured" tritium recovery data. Both these data sets are shown in Figure 2(a). The time axis was then shifted to align  $t=0$  to the peak of the second curve. The re-zeroed recovery-rate curve was



integrated and normalized to obtain fractional release  $f(t)$  as a function of time, and then differentiated in the proper manner to obtain  $d\ln(f)/d\ln(t)$ . The result, shown in Figure 2(b), demonstrates that the derivative rapidly (within a few time constants) drops from 1 to a value somewhat larger than 0.5 and then decreases only slowly toward 0.5.

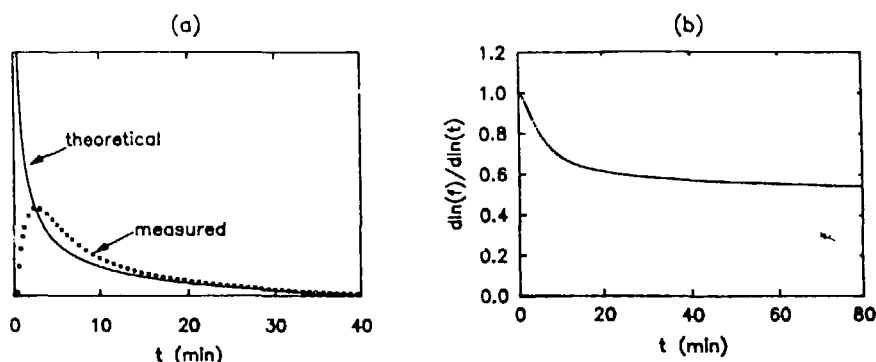


Fig. 2 Diffusion-controlled release: (a) shows the theoretical recovery rate predicted by equation 3 ( $D/a^2 = 1 \times 10^{-5} \text{ min}^{-1}$ ), and the recovery rate that an ion chamber with the response curve shown in Figure 1 would measure. The vertical axis is tritium concentration or tritium recovery rate in arbitrary units; (b) shows  $d\ln(f)/d\ln(t)$  for the 'measured' curve, after shifting the time axis to the peak maximum.

The shape of the logarithmic derivative for first-order desorption control of tritium release is markedly different. Procedures similar to those described above for diffusion control were performed using equation 8; Figures 3(a) and (b) show the results. In this case, the derivative drops smoothly from 1 towards 0. Figures 4(a) and (b) show the results for second-order desorption. Again, the derivative drops smoothly from 1 towards 0, but more slowly.

Different values of  $D$  and  $k$  for Figures 2-4 were tested; qualitatively, the results are similar. Thus, the shape of the logarithmic derivative over long times can be used to distinguish between diffusion- and desorption-controlled release.

4. APPLICATION TO  $\text{LiAlO}_2$

Lithium aluminate samples were irradiated at Chalk River Laboratories, and tritium release measured out-reactor. The samples were 55-65% T.D.,  $1.2 \mu\text{m}$  grain size (average), 50-100 mg, and were irradiated to generate 20-40 mCi/g ( $1 \text{ Ci} = 37 \text{ GBq}$ ) tritium. They were vacuum annealed ( $3 \times 10^{-2} \text{ Pa}$ ) in silica glass tubes at 873 K for one hour and then sealed for irradiation without

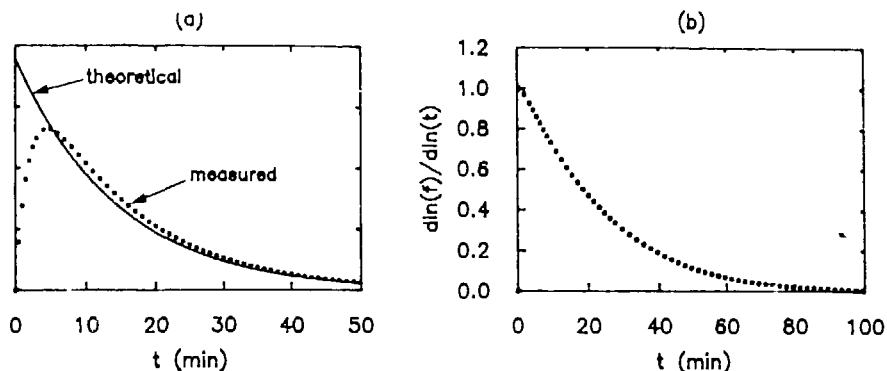


Fig. 3 First-order desorption-controlled release; (a) shows the theoretical recovery rate given by equation 4 ( $k = 7 \times 10^{-2} \text{ min}^{-1}$ ), and the recovery rate that an ion chamber would measure. As for Figures 2 and 4, this was obtained by convoluting the theoretical curve with the response curve shown in Figure 1; (b) shows  $d\ln(f)/d\ln(t)$  for the measured curve, after shifting the time axis to the peak maximum.

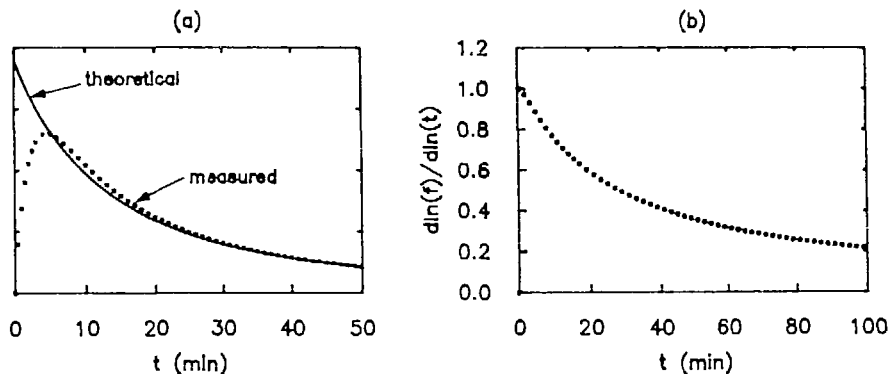


Fig. 4 Second-order desorption-controlled release ( $k = 4 \times 10^{-2} \text{ min}^{-1}$ ). The information corresponds to that of Fig. 3 for first-order desorption.

exposure to air. The apparatus for heating the specimens and measuring tritium release is described in Reference (4). Only the reduced form ( $HT$  and  $T_2$ ) of the tritium was measured on-line (in an ion chamber), since the tritium and carrier gas were first passed through an ethylene glycol bubbler to remove the tritiated water. However, for all samples, except one tested in pure He, the release was predominantly (75-99%) the reduced form. Figures 5 and 6 show the release data for two samples. The time axis was shifted to the peak maximum for each sample; release prior to that time was ignored; and the release curve was integrated to obtain fractional release versus time. ( $f$  need only be the integrated, non-normalized release.)

Figures 5 and 6 also show best fits of the recovery-rate data to the predictions of first-order desorption. The fits are excellent. Attempts to fit the data to second-order desorption or diffusion were less successful. Similar results were obtained for the other samples. The figures also show plots of  $d\ln(f)/d\ln(t)$  for the two samples. First, note that the slope is negative everywhere for both samples; this means that relation (6) is satisfied. Second, as expected, the derivative tends to 1 as  $t$  goes to 0; this provides no information about the release-controlling mechanism. However, the overall shape of the curve is similar to that in Figure 3, implying that first-order desorption is the rate-controlling mechanism. Thus, the evidence is strong that, for these samples, irradiation and release conditions, the kinetics of tritium release were controlled by first-order desorption from the surface. The value of the desorption coefficient  $k$  for the sample shown is given in the figure.

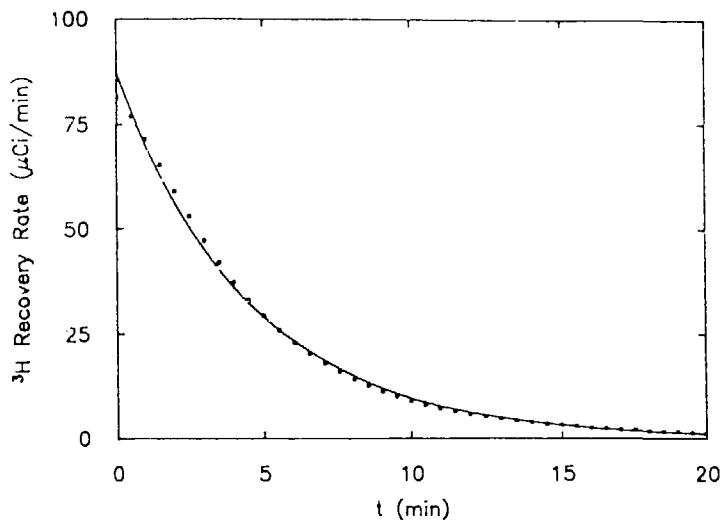
Also, note that for first-order desorption, the desorption coefficient (and the time constant for release) is independent of the original tritium concentration. However, the same is not true for second-order desorption. Here, the desorption coefficient (and release time constant) does depend on the original tritium concentration. The quantity  $k/A$ , where  $A$  is the original tritium concentration, is independent of the original level. Appendix 2 demonstrates this point.

## 5. CONCLUSIONS

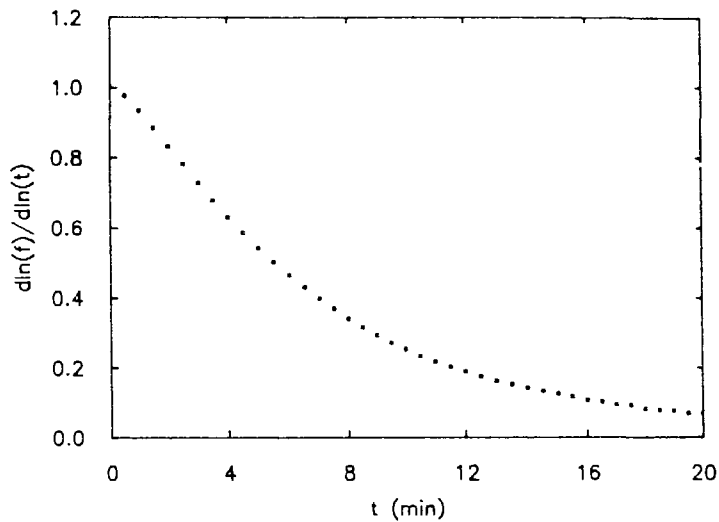
- $\lim_{t \rightarrow 0} \frac{d\ln(f)}{d\ln(t)} = 1$  for any shape of tritium-release curves

where  $f$  is the fractional tritium release. This limit is therefore not useful in distinguishing diffusion-control from desorption-control.

- Examining the behaviour of  $d\ln(f)/d\ln(t)$  for long times does provide information on the controlling release mechanism.
- The logarithmic derivative plots,  $d\ln(f)/d\ln(t)$ , for tests on  $LiAlO_2$  indicated that release was controlled by first-order desorption. The recovery-rate data matched the first-order release-rate predictions well.

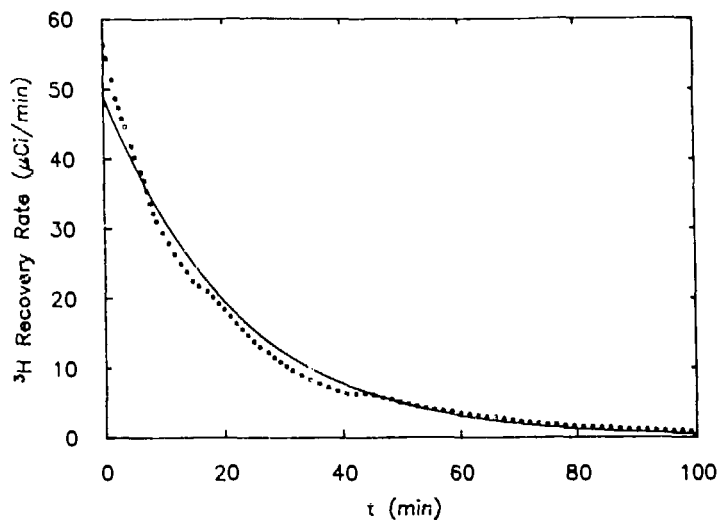


(a)

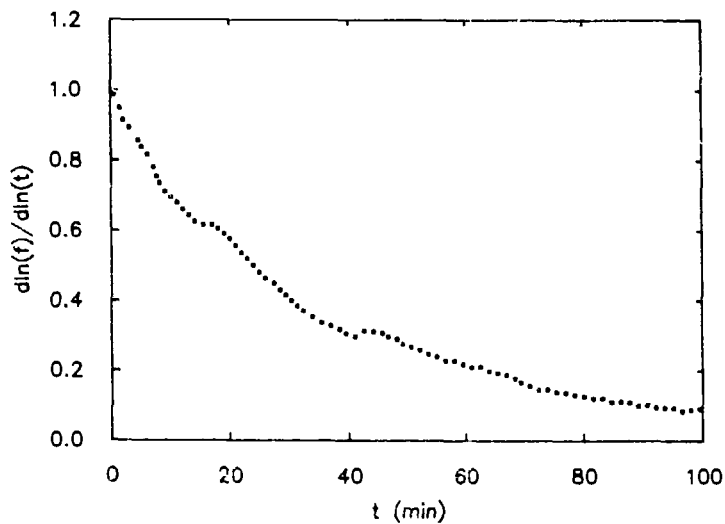


(b)

Fig. 5  $\text{LiAlO}_2$  Sample 1, 55% T.D., tested at  $600^\circ\text{C}$  with  $\text{He}-0.1\% \text{H}_2$  sweep gas flowing at  $100 \text{ mL}/\text{min}$ ; (a) shows the recovery rate (dots), with  $t=0$  shifted to the peak maximum, and the best two-parameter fit (solid line) of equation 10 for first-order desorption ( $k = 0.22 \text{ min}^{-1}$ ); (b) shows  $d\ln(f)/d\ln(t)$ , resembling the curve shown in Figure 3(b)



(a)



(b)

Fig. 6  $\text{LiAlO}_2$ , Sample 2, 55% T.D., tested at  $550^\circ\text{C}$  with  $\text{He}-0.1\% \text{H}_2$  sweep gas flowing at  $100 \text{ mL}/\text{min}$ ; (a) shows the recovery rate (dots) after the time axis was shifted 5.5 min to the peak maximum; the best fit (solid line) of equation 10 gave  $k = 4.7 \times 10^{-2} \text{ min}^{-1}$ ; (b) shows  $d\ln(f)/d\ln(t)$ .

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APPENDIX 1

Evaluation of  $\lim_{t \rightarrow 0} \frac{d \ln(f)}{d \ln(t)}$

As shown in the text, when measuring tritium release rate from lithium ceramics, ion chamber (or proportional counter) readings will always increase from zero to a maximum, and then decrease. When evaluating the above derivative, the time scale is usually shifted so that  $t=0$  corresponds to the peak maximum, but any shift is acceptable in the following analysis. For times near  $t=0$ , the release rate  $r(t)$  can be written as a polynomial:

$$r(t) = a_0 + a_1 t + \dots$$

At time  $t$ , the fraction of recovered tritium is:

$$\begin{aligned} f(t) &= \frac{1}{A} \int_0^t r(t) dt \\ &= \frac{1}{A} \left( a_0 t + \frac{a_1 t^2}{2} + \dots \right) \end{aligned}$$

where  $A$  is the total tritium recovered. Then,

$$\begin{aligned} \frac{d \ln(f)}{d \ln(t)} &= \frac{t}{f} \frac{df}{dt} = \frac{At}{\left( a_0 t + \frac{a_1 t^2}{2} + \dots \right)} \cdot \frac{1}{A} (a_0 + a_1 t + \dots) \\ &= \frac{t(a_0 + a_1 t + \dots)}{t(a_0 + \frac{a_1 t}{2} + \dots)} \end{aligned}$$

Therefore,  $\lim_{t \rightarrow 0} \frac{d \ln(f)}{d \ln(t)} = 1$

This holds for any shape of the tritium recovery curve. Note that the only restriction is that the  $t=0$  point not be selected so that  $a_0=0$ , i.e., at a point where the ion chamber reading is zero. Also note that normalization of  $f$  is not required, since the log derivative is independent of the normalization factor. Even an incorrect normalization factor would not affect the log derivative.

The logarithmic derivative is most easily calculated using the following relationship:

$$\frac{d \ln(f)}{d \ln(t)} = \frac{t}{f} \frac{df}{dt} = \frac{t}{f} r(t)$$

where, in this case,  $f$  is not normalized so that its derivative is  $r(t)$ . Thus, no derivatives actually need to be calculated.

## APPENDIX 2

### The Second-Order Desorption Process: What Parameter is Constant?

Second-order desorption of tritium from a surface occurs when a tritium atom (or ion) must combine with another atom (or ion) to desorb. When the initial concentration of tritium is high, combination on the surface occurs relatively quickly and a specified fraction (e.g., 2/3) of the initial tritium will be released quickly. However, if the initial concentration is low, the combination rate is low, and it will take much longer to release the same fraction. In other words, the time constant for release and, therefore, also the desorption coefficient depend on the initial concentration.

To determine this relationship, assume that two tests on the same sample with different initial tritium contents,  $A$  and  $A'$ , yield the desorption coefficients  $k$  and  $k'$ . The release rates at any time  $t$ , measured from the start of the respective tests, are obtained from equation 11 in the text:

$$r(t) = \frac{Ak}{(1 + kt)^2}$$

and

$$r'(t) = \frac{A'k'}{(1 + k't)^2}$$

Integration of both formulas from 0 to infinity yields, as expected,  $A$  and  $A'$ , the total amounts of tritium in the two tests.

Without loss of generality, assume that  $A' < A$  and, therefore, that at some time,  $t_1$ , after the start of the first test, the total amount of tritium remaining in the sample is  $A'$ , the original amount in the second test.

This can be expressed by:

$$A' = \int_{t_1}^{\infty} \frac{Ak}{(1 + kt)^2} dt = \frac{Akt}{(1 + kt)} \Big|_{t_1}^{\infty} = A - \frac{Akt_1}{1 + kt_1}$$

or

$$A' = \frac{A}{1 + kt_1} \tag{A1}$$

But the release rates must also be identical; i.e.,

$$r(t_1) = r'(0)$$

or,

$$\frac{Ak}{(1 + kt_1)^2} = A'k' \tag{A2}$$



Solving equation A1 for  $(1 + kt_1)$  and inserting this into equation A2 gives:

$$\frac{k}{A} = \frac{k'}{A'} \quad (A3)$$

i.e., the desorption coefficient divided by the amount of tritium in the sample is a constant for the system, independent of the initial amount of tritium in the sample.

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