Determination of the Absolute Activity of Solid Tritium Samples

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It is shown that the absolute specific beta activity of tritium in solid samples of finite thickness can be accurately determined with 2π internal gas-flow counters. The effects of self-absorption and back-scattering of tritium betas are discussed.

The new simple methods for direct labeling of organic compounds with radio-active hydrogen (for references see Ref.[1]) in combination with the low price of the latter is causing a rapid increase in the use of tritium-tagged organic compunds. This calls for simple methods of measuring tritium activities. The most commonly used seems to be the counting of gaseous samples in various ionization chambers and dissolved samples in liquid scintillation counters (cf.e.g. Refs.[2,3]). However, these methods require special or expensive equipment, usually not available in normal radiometric laboratories. Because of the low energy of the β- radiation of ^3T (upper energy limit 18 keV), measurements on solid samples present some difficulties, but these can usually be overcome by using internal gas flow counters and a refined sample preparation technique. So far only four papers [4-7] seem to have dealt with this problem in some detail. In none of these papers is the absolute determination of tritium activity discussed, and the results do not seem generally applicable to all kinds of solid tritium samples. In the present paper these problems will therefore be somewhat more extensively treated.

VARIABLES IN ABSOLUTE β-COUNTING

Zumwalt [8] has summarized the different variables which have to be considered in the determination of absolute β-activity of solid samples. Here, only the case of using internal gas-flow counters will be discussed, which limits the number of variables. The correction factors are

f_e, the efficiency of the measuring device to register all β-particles entering the detector;

f_r, the combined resolving time of the detector and the electronic and mechanical components;

f_g, the geometry of the detector viewed from the radiation source;

f_b, the back-scattering of radiation from the backing material into the counter;

f_s, the self-absorption and back-scattering of the β-radiation in the sample.

If the true specific activity is S dpm/g (disintegrations per minute per gram), and the measured activity is I cpm (counts per minute) in a sample of weight m grams, the following relation holds:

$$S = I/m \cdot f_e \cdot f_r \cdot f_g \cdot f_b \cdot f_s \quad \text{dpm/g} \tag{1}$$

When a GM-counter shows a flat plateau (*i.e.* pulse frequency is independent of anode voltage) it is generally assumed that all β-particles entering the detector are registered [9]. This is certainly true if the pulse frequency is so low that no resolution loss is obtained (*i.e.* if $f_r = 1$). The same reasoning should hold when the detector, instead of a GM-tube, is a proportional tube. Experiments made by the author have given identical results for internal gas-flow GM-counters (helium-*iso*butan mixture) and proportional counters (argon-methane mixture). Thus if solid samples are measured in the sensitive volume of these detectors, the factor f_e is very close to 1, when $f_r = 1$ and the tubes are operated at the plateau.

If flat planchettes are used to support the radiation source placed in the sensitive volume of a 2π internal gas-flow counter, the factor f_g can be put equal to 0.5.

When the radiation source is outside the sensitive volume of the detector, the geometry of the source in relation to the detector has to be calculated (*cf. e.g* Ref.[10]). A more accurate method is to use a calibrated radiation source in the actual geometry, and to determine $f_g \cdot f_e$ in one step; this value of $f_g \cdot f_e$ is only strictly valid for the specific isotope used.

The fraction of β-radiation scattered from the backing material into the detector depends on the β-spectrum, the atomic number and thickness of the backing material. When the thickness of the backing material is $> R_o/3$, where R_o is the maximum range of the β-particles, maximum ("saturation") back-scattering is obtained. Since accurate predictions of the value of the saturation back-scattering factor, f_b, are difficult to make for low β-energies (*cf. e.g.* Ref.[11]), this factor is most easily determined experimentally.

Fairly simple equations can be given for the dependence of the self-absorption of the mass density of the sample. The derivation and use of these equations have been discussed by several authors (*e.g.*Refs.[12–14]). However, in ordinary experimental work with thick samples it is generally not possible to distinguish between self-absorption and back-scattering in the source [16]. In order to make absolute determination of β-activity in a given sample, experimentally determined values of f_s should be used.

<div style="text-align:center">EXPERIMENTAL</div>

<div style="text-align:center">S a m p l e   p r e p a r a t i o n</div>

Solid samples. The samples prepared for solid counting were obtained by evaporating solutions of tritiated *p*-aminosalicylic acid (PAS) [1] in 96 % ethyl alcohol. The positions of the tritium atoms in PAS are not definitely known, but they are non-labile in water
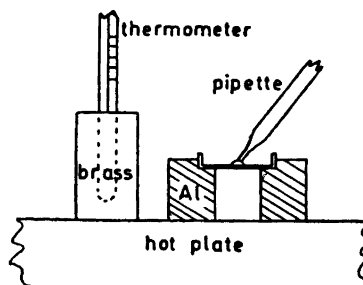
||*Fig. 1.* Arrangement for sample
preparation.

of pH 3—7. It is believed that in the alcoholic solutions no exchange of tritium takes place between the PAS and the solvent. 96 % ethyl alcohol was used because no solid residues were left after its evaporation.

Fig. 1 shows the arrangement used to prepare the samples [17]. In order to obtain reproducible samples it is important to keep the hot plate and aluminium ring at the correct temperature (in this case at 55°C), and to put the cold sample-pan on the aluminium ring just before adding the 0.1 ml of the solution through the pipette. The sample-pan should be kept perfectly horizontal and any rapid airflow around it should be avoided. Under these circumstances, there is formed a droplet, which evaporates slowly from its rim. The dry samples obtained had a diameter of 13 ± 1 mm.

The activities measured never exceeded 5 000 cps, which corresponded to a sample thickness of about 100 $\mu g/cm^2$. In order to measure on still thicker samples, inactive PAS was added to the active alcohol solution, and appropriate corrections for the dilution of the active PAS were made.

Gas samples. Gas samples were prepared by converting the tritium in solid tritiated PAS to water. This water was then reduced with magnesium to produce hydrogen for measurements in a GM-counter, according to Melander [18].

Counting arrangements

For the measurements on solid samples an internal gas-flow proportional counter (model PC-3, Nuclear Measurements Corp., Indianapolis) with 90 % A + 10 % CH_4 was used. The resolution loss was around 1 % at 5 000 cps; since higher activities never were measured, corrections for resolution loss could be neglected.

Before the introduction of a sample into the counter, the background was measured. For each sample 5—10 measurements were made to check that the counter worked properly; between each measurement, the counting tube was flushed with the counting gas. In general it was found that in such a sequence of measurements, the activity first rose slightly and then decreased. The rise is believed to be due to insufficient flushing in the beginning, and the decrease due to mechanical loss of sample from the sample-pan because of the flushing. This assumption is supported by the fact that the back-ground count rose steadily with each new sample measured. When the back-ground had reached ∼1 000 cpm, the counting chamber was removed and cleaned, after which the background usually dropped to the ordinary value of ∼200 cpm (unshielded). The difference between the highest and the lowest activity measured on one sample in this way never amounted to more than 7 % and in general was much less. The average between the two highest values was used.

For comparison with the results obtained on solid samples with the proportional counter, an internal gas-flow GM-counter (Model SC-16, Tracerlab Inc., Boston) using 99 % helium + 1 % *iso*butane was used in a few experiments with samples of low activity. Results completely consistent with those of the proportional counter were obtained when identical samples were used in both counters.

To check the activites obtained by the method described in this paper, a GM-counter especially made for tritium-gas samples [18] was also used (propane-hydrogen mixture at about 100 mm Hg).

Table 1. Measured activity, I, as a function of sample weight, m, for various backing materials; sample area is 1.3 ± 0.2 cm².

Sample weight	Aluminium backing		Stainless steel backing		Platinum backing	
m μg	I cpm $\times 10^{-3}$	$I/m \dfrac{\text{cpm}}{\mu\text{g}}$	I cpm $\times 10^{-3}$	$I/m \dfrac{\text{cpm}}{\mu\text{g}}$	I cpm $\times 10^{-3}$	$I/m \dfrac{\text{cpm}}{\mu\text{g}}$
2 000	712 ± 4	356 ± 2	708 ± 4	354 ± 2	980 ± 5	490 ± 2
1 000	810 ± 2	810 ± 2	880 ± 3	880 ± 3	1 070 ± 3	1 070 ± 3
460	720 ± 1	1 570 ± 3	698 ± 1	1 520 ± 3	837 ± 2	1 820 ± 4
90	245 ± 1	2 720 ± 5	244 ± 1	2 720 ± 5	290 ± 1	3 330 ± 7
9	35.0 ± 0.2	3 780 ± 2	420 ± 0.2	4 670 ± 2	44.5 ± 0.2	4 950 ± 2
0.9	4.2 ± 0.1	4 670 ± 90	4.43 ± 0.1	4 930 ± 90	5.38 ± 0.1	5 990 ± 120
0.09	0.445 ± 0.04	4 950 ± 500	0.537 ± 0.05	5.970 ± 600	0.60 ± 0.06	6.670 ± 670

RESULTS

The experimental data. The results obtained are collected in Table 1. The errors given are only statistical (root mean square), owing to the number of counts measured. The error in the sample weight, which is not considered in the table, is assumed to be less than 10 %. The sample areas are not known more accurately than 1.3 ± 0.2 cm². In Fig. 2, the activity, I (cpm), is plotted against the sample weigth m (μg) on a logarithmic scale. Since the values for the various backing materials lie fairly close to each other, the scale for the three sets of data has been displaced one log unit each along the ordinate. In Fig. 3 the relative activity, I/m, is plotted against log m. The difference between the three backing materials at low sample weights is obvious here. The use of the curves in Figs. 2 and 3 shall be further discussed below.

Calculations. It has been shown (*e.g.* Refs.[12-15]) that the self-absorption of β-radiation can be well described by the equation

$$\frac{A_x}{A_0} = \frac{1 - e^{-\mu x}}{\mu x} \tag{2}$$

where A_x is the activity of a given amount of a radioactive isotope contained in a sample of thickness x mg/cm² (for $x = 0$, the activity is A_0) and μ is the absorption coefficient. If it is assumed that the sample area is constant, this relationship can be rewritten

$$I = \frac{A_0}{\mu} (1 - e^{-\mu m}) \tag{3}$$

where $I = m \cdot A_x$ is the activity from the sample area containing m mg sample (the dimension of μ in eqn. 3 is weight^{-1}). Thus if log I is plotted against log m, a curve should be obtained with the two asymptotes

$$\lim_{m \to 0} \log I = \log A_0 + \log m \tag{4 a}$$

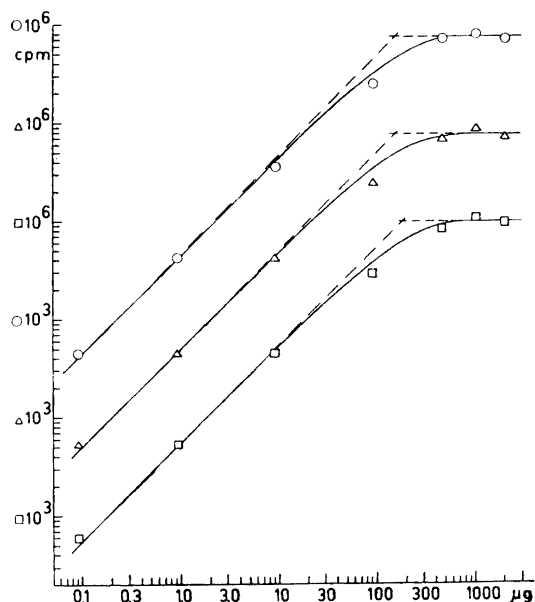$$\lim_{m \to \infty} \log I = \log A_0 - \log \mu \tag{4 b}$$

Fig. 2. Measured activity, I cpm, as a function of sample weight, m μg, at constant specific activity. The curves according to eqns. 3 and 4 are displaced one log unit along the ordinate for each backing material (O aluminium, △ stainless steel, □ platinum backing).

The intercept between these two asymptotes occurs at log $m = - \log \mu$. This point is easy to determine in a log I *versus* log m plot, since the asymptotes intersect each other at an angle of 135°.

Fig. 2 has been used to determine μ (in μg^{-1}) by this method as well as A_0; the asymptotes are given as dotted lines in the figure. The values obtained are given in Table 2, together with estimated errors. With these values of μ and A_0 introduced into eqn. 3, log I has been calculated as a function of log m, and the result thus obtained is given in the solid curves in Fig. 2.

Table 2. Calculations of μ (in μg^{-1}) and A_0 (in cpm) from Figs. 2 and 3.

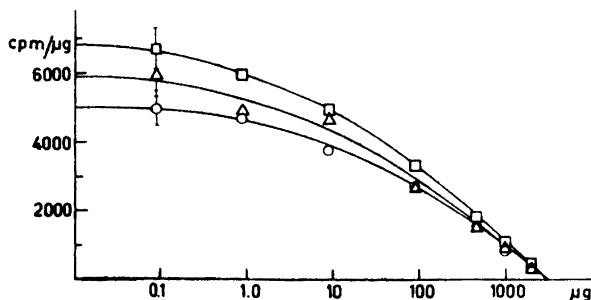| Value	according to	Backing material		
		aluminium	stainless steel	platinum
$1/\mu$	Fig. 2	150 ± 30	145 ± 20	180 ± 20
A_0/μ	» 2	$(750 \pm 50) \; 10^3$	$(770 \pm 70) \; 10^3$	$(1\,000 \pm 70) \; 10^3$
A_0	» 2	$5\,000 \pm 400$	$5\,300 \pm 500$	$5\,600 \pm 400$
A_0	» 3	$5\,000 \pm 200$	$5\,900 \pm 400$	$6\,800 \pm 200$

Fig. 3. Apparent specific activity, I/m (cpm/μg), as a function of sample weight, m (μg), for various backing materials (O aluminium, $\triangle$ stainless steel, $\square$ platinum).

According to eqn. 4a, A_0 can also be obtained from the plot in Fig. 3. The inaccuracy in the A_0-value obtained for $m \to 0$ is rather large; the estimated values are given in Table 2.

The difference between the A_0-values obtained with aluminium, stainless steel and platinum as backing material must be due to the back-scattering of the radiation by these materials. The back-scattering factor, f_b, has been calculated as a function of the atomic number of the backing material in Fig. 4. This has been done by first calculating the relative backscattering factor (f_b') in stainless steel and platinum towards aluminium ($f_b' = 1.00$) and the displacing the curve f_b' *versus* atomic number, Z, so that the extrapolated curve starts with $f_b = 1.00$ at $Z = 0$. In these calculations, the A_0-values obtained from Fig. 3 have been used.

DISCUSSION

The self-absorption factor. As an average of the $1/\mu$-values in Table 2 one obtains 160 ± 25 μg. Since the sample area is 1.3 ± 0.2 cm^2, this corresponds to $1/\mu = 120 \pm 25$ μg/cm^2. From the relationship [13] $d_{1/2} = 0.693/\mu = 0.139$ R_0, where $d_{1/2}$ is the half-value thickness of the beta radiation, one thus obtains $d_{1/2} = 0.08 \pm 0.02$ mg/cm^2 and $R_0 = 0.6 \pm 0.1$ mg/cm^2. These values should be compared with the directly measured values $d_{1/2} = 0.07$ mg/cm^2 (giving $R_0 = 0.5$ mg/cm^2)[19] and $R_0 = 0.23$ mg/cm^2 (giving $d_{1/2} = 0.032$ mg/cm^2)[20], and the calculated value $R_0 = 0.7$ mg/cm^2 (giving $d_{1/2} = 0.10$ mg/cm^2) from the Glendenin [21] energy-range relation. Though the agreement between these three latter values is not remarkably good, two [19,21] of them agree well with the value obtained here.

It is seen from Fig. 2 that the experimental points at intermediate sample weights ($\sim$ 100 μg) fall below the theoretical curve given by eqn. 3. The reason for this may be due partly to the fact that eqn. 2 is only strictly valid for collimated radiation, and partly to the interrelation between self-absorption and back-scattering (*cf.* Ref.[16]). As the sample thickness increases, part of the radiation is back-scattered by the sample itself rather than by the backing material and, since the sample material has a lower back-scattering power (lower average atomic number) than the backing material, less radiation will
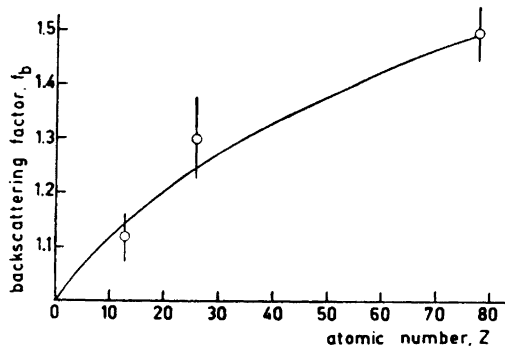
Fig. 4. Saturation back-scattering factor, f_b, as a function of the atomic number Z of the backing materials.

be scattered back into the counter. The back-scattered radiation has a much lower average energy than the unscattered beta-radiation, and is thus more easily absorbed in the sample, which lowers the fraction of back-scattered radiation reaching the sensitive volume of the counter. This is clearly indicated in Fig. 3, which shows that with increasing sample weight, the activity measured becomes more and more independent of the orginal backing material.

Thus the increasing sample weight causes the experimental points to become lower than would have been the case if only self-absorption was operating. The horizontal asymptote should, in such a case, have been situated higher than is shown in Fig. 2, and consequently a higher $1/\mu$-value would also have been obtained. On the other hand, the experimental points at low m-values in Fig. 2 do not fall exactly on the straight line, which indicates that the line of 45° slope should be somewhat displaced to the left (that this is true is seen
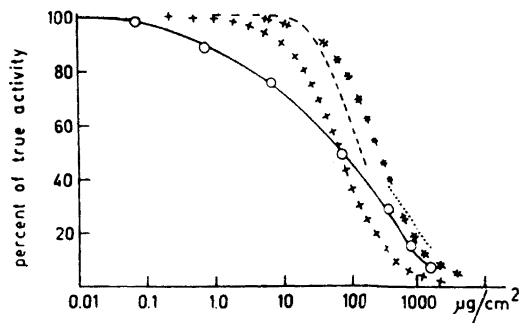

Fig. 5. Percentage of true activity measured from tritium samples of various surface thickness. The experimental results in this work is denoted by --o--o--, curves calculated according to eqn. 2 by + + + + for $R_0 = 0.2$ and by ⧺⧺⧺⧺ for $R_0 = 0.8$ mg/cm², while — — — — indicates results by Jackson and Lampe [7], and . . . . by Eidinoff and Knoll [4].

Table 3. Calculations of percent of true activity measured from samples of various thickness (in $\mu g/cm^2$). The A_0:values used are taken from Fig. 3, as given in Table 2.

m μg	m/a $\mu g/cm^2$	$100\ I\ A_0^{-1}\ m^{-1}$ for various backing materials			
		aluminium	stainless steel	platinum	mean value
2 000	1 540	7 %	6 %	7 %	7 %
1 000	770	16 »	15 »	16 »	16 »
460	350	31 »	26 »	27 »	28 »
90	70	54 »	46 »	49 »	50 »
9	7	76 »	79 »	73 »	75 »
0.9	0.7	94 »	84 »	88 »	89 »
0.09	0.07	99 »	101 »	98 »	99 »
(0.0)	(0.0)	(100) %	(100) %	(100) %	(100) %

from Fig. 3). It is difficult to estimate to what extent these two corrections affects $1/\mu$, but it is believed that the true $d_{1/2}$-and R_0-values are approximately equal to those obtained from Fig. 2 (*i.e.* $d_{1/2} = 0.08 \pm 0.02$ mg/cm², $R_0 = 0.6 \pm 0.1$ mg/cm²).

A serious consequence of this is that it points out the difficulties in using eqn. 2 for the determination of the relation between measured and true activity. As has been pointed out by Glendenin and Solomon [15], it is advisable to make self-absorption curves for each particular experimental condition if any accuracy is desired. The self-absorption factor, f_s, is therefore best obtained from curves like those in Fig. 3.

Using these data

$$f_s = \frac{100 \cdot I}{A_0 \cdot m}\ \% \tag{5}$$

has been calculated as a function of m/a, (Table 3, and solid line in Fig. 5) where a is the area of the sample.

In Fig. 5, the experimental results obtained by Eidinoff and Knoll [4] (dotted curve) and Jackson and Lampe [7] (dashed curve) are also given. Considering the experimental difficulties, the agreement with the former investigation seems reasonable, but the deviation from the latter investigation is very great. The reason for this deviation may partly be that it is easier to obtain well-defined and even samples with the substances (triglycerides, fatty acids and soaps) investigated by Jackson and Lampe, than with PAS, which tends to form small aggregates of micro crystals. This may also explain why Jackson and Lampe obtained infinitely thin samples at a surface density of $\lesssim 10\ \mu g/cm^2$, while in our case this was not obtained until $\lesssim 0.1\ \mu g/cm^2$. However, the steeper rise of the upper part of the curve given by Jackson and Lampe compared with that of the theoretical curve lacks explanation.

The back-scattering factor. The discussion above has indicated that the A_0-values obtained at infinite sample thickness from Fig. 3 are more reliable than those obtained from Fig. 2. If a comparison is made with the results

obtained by Yaffe and Justus [11], the back-scattering factor obtained here seems far too high. However, from Seliger's [22] angle-energy relationship for scattered radiation one is bound to explain this discrepancy as being due to the use of different measuring equipment, *i.e.* in Yaffe's case, the use of low geometry and absorbing materials between the sample and the counter, which removes a considerable fraction of the soft scattered radiation.

Conclusion. Eqn. 1 has been used for the determination of the absolute specific activity, S, of a tritium sample. It has been pointed out that in a 2π internal gasflow proportional counter, the geometry can be assumed to be 50 % (*i.e.*, $f_g = 0.5$) and the efficiency 100 % ($f_e = 1$) when the counter is operated in the plateau at a reasonably low counting rate ($f_r = 1$). Methods for the determination of self-absorption (f_s) and back-scattering (f_b) have been described.

Under these conditions, S was determined for a tritiated solid PAS-sample, giving a result of 790 $\pm$ 40 dpm/mmole hydrogen. A fraction of the same sample was then analyzed for tritium as hydrogen gas internally in a GM-counter, giving 860 $\pm$ 120 dpm/mmole. Considering the uncertainties caused by all correction factors in eqn. 1, the agreement is very good, indicating the usefulness of the method described in this paper for rapid and absolute determination of tritium activities in solid samples.

REFERENCES

1. Rydberg, J. and Hanngren, Å. *Acta Chem. Scand.* 12 (1958). 332.
2. Grenan, M. and Vialland, R. *J. Chim. Phys.* 49 (1952) 623.
3. Okita, G. T., Spratt, J. and Leroy, G. V. *Nucleonics* 14 No. 3 (1956) 76.
4. Eidinoff, M. L. and Knoll, J. E. *Science* 112 (1950) 250.
5. Gray, I., Ikeda, S., Benson, A. A. and Kritchevsky, D. *Rev. Sci. Instr.* 21 (1950) 1022.
6. Jenkins, W. A. and Yost, D. M. *J. Chem. Phys.* 20 (1952) 538.
7. Jackson, F. L. and Lampe, H. W. *Anal. Chem.* 28 (1956) 1735.
8. Zumwalt, L. R. *MDDC*-1346 (1947).
9. Frisby, J. H. and Roaf, D. *Proc. Phys. Soc. (London)* 64B (1951) 169.
10. Gleason, G. I., Taylor, J. D. and Tabern, D. L. *Nucleonics* 8 No. 5 (1951) 12.
11. Yaffe, L. and Justus, K. M. *J. Chem. Soc. Suppl.* 1949 S341.
12. Henriques, F. C., Jr., Kristiakowsky, G. B., Margnetti, C. and Schneider, W. G. *Ind. Eng. Chem., Anal. Div.* 18 (1946) 349.
13. Libby, W. F. *Anal. Chem.* 19 (1947) 2.
14. Schweitzer, G. K. and Stein, B. R. *Nucleonics* 7 No. 3 (1950) 65.
15. Glendenin, L. E. and Solomon, A. K. *Science* 112 (1950) 623.
16. Nervik, W. E. and Stevenson, P. C. *Nucleonics* 10 No. 3 (1952) 18.
17. Olausson, B. and Rydberg, J. *FOA Report* 10092—8509, 1954.
18. Melander, L. *Acta Chem. Scand.* 2 (1948) 440.
19. Dorfman, L. M. *Phys. Rev.* 95 (1954) 393.
20. Brown, S. C. *Phys. Rev.* 59 (1941) 954.
21. Glendenin, L. E. *Nucleonics* 2 No. 1 (1948) 12.
22. Seliger, H. H. *Phys. Rev.* 88 (1952) 408.