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The Quantitative Estimation of the Activity of Beta Particle Emitters

by

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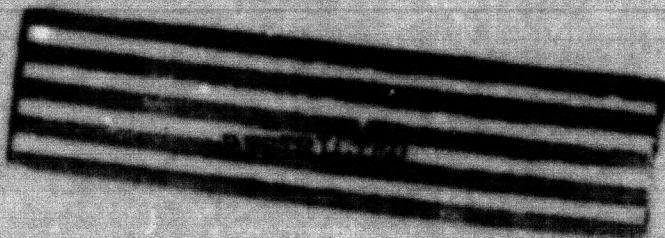
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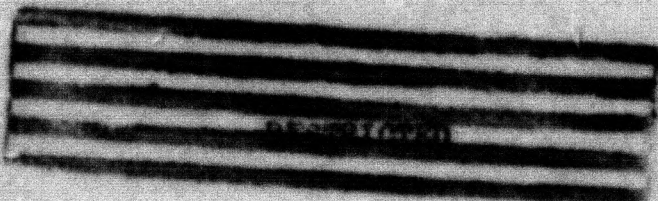


Abstract

In estimating the activities of β -emitting materials used in the Biology Section, most measurements were made with Geiger-Mueller counters, although Lauritsen electroscopes were used in early work. All samples were mounted on flat porcelain capsules.

In the determination of absolute activity, errors arising from absorption and scattering were minimized by maintaining uniform conditions of measurement. Absolute standardization of the Geiger-Mueller counters was accomplished using both Ux_2 and Ra E, and U_3O_8 reference standards were calibrated against the absolute standards. Methods of preparing the standards were developed. Values derived from the Ra E standards exceeded those from Ux_2 by 8 per cent. Using the ratio of the measured activity to the absolute activity of the standards, it was possible to correct the measured activities of unknown samples to absolute activities. It is probable that the uncertainty in the determination of the absolute activity value is less than ten per cent.

Lauritsen electroscopes were calibrated against samples accurately measured with Geiger-Mueller counters. Sensitivities for various isotopes on the electroscopes used were of the order of one division per second per microcurie.



The Quantitative Estimation of the Activity of Beta Particle Emitters

by

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 and Sheldon H. Himmelfarb

(with the assistance of Clifford Nordeen)

1. Introduction

For the radio-toxicology studies of the Experimental Biology Section, absolute activity determinations were needed to establish the doses to animals. This paper was written to describe the methods used for the estimation of absolute beta ray activities. The toxicology reports will, therefore, not repeat this information. The paper includes methods of preparing absolute standards of U_2 and Ra E, and permanent reference standards of U_3O_8 ; the calibration of Geiger-Mueller counters; and the standardization of Lauritsen electroscopes. Geiger-Mueller counters have been used exclusively since a few months after the biological program was begun, and the major portion of the report deals with the use of this instrument.

Since the problem of routinely handling large samples of ashed tissue is essentially unique with the Biology Section, the method of mounting samples differs from that used by others⁽¹⁾. Ashed tissue samples are conveniently mounted on small flat porcelain evaporation dishes referred to as capsules. (Two sizes are used; the small capsules are 33 mm in diameter with walls 10 mm high; the large are 45 mm in diameter with 12 mm walls). In order to maintain the same conditions as closely as possible, standards have been mounted in a similar manner.

For measuring activity, the capsules are placed on holders 6.5 cm long and 8.2 cm wide. The holder consists of a card to which is attached a Lucite slab

1/4" thick with a centered hole large enough to hold the corresponding size of capsule. The holders are supported under the measuring device (counter or electroscopes) by a set of aluminum brackets shelves).

2. Calibration of the Geiger-Mueller Counter

2.1 Apparatus: The apparatus used by the Biology Section consists of a thin mica window counter tube mounted in a cylindrical lead shield above a set of aluminum brackets. The holder containing the capsule and active material is introduced through a door near the bottom of the lead shield. A detailed description of the counter tube, amplification circuit, and the counter circuit may be found elsewhere ⁽²⁾.

2.2 Geometry: In measuring the activity of a β -emitting material with the apparatus described, only a fraction of the total number of disintegrations is recorded. Corrections can be made for self-absorption and for absorption by intervening materials; but there remains the "geometry", here defined as the counting efficiency at zero absorber, that is, the proportion, after correcting for absorption, of the total number of disintegrations per unit time that are actually counted. The determination of this "geometry" is somewhat more complex than a determination of the solid angle subtended by the number of particles actuating the counter. For this reason, geometry is ordinarily determined empirically by measuring the activity of known standards and determining the ratio of the measured activity (corrected to zero absorber) to the calculated total activity.

In this laboratory, geometry has been established for β -counters by use of absolute standards consisting of pure U^{235} which was separated from a solution U^{235} - refers to a mixture of U^{235} and U^{238} .

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of a measured weight of uranium, or of radium E, the activity of which was determined by α counts of radium F under known geometry. Reference standards of U_3O_8 calibrated against the absolute standards have been prepared for routine use.

Corrections for absorption are less difficult to make when samples are read on higher shelves, since on higher shelves the absorption curve plotted on semi-log paper becomes more nearly linear and the extrapolation to zero absorber is more reliable⁽³⁾. In most cases, therefore, experimental samples were measured on the higher shelves when possible.

Counting on lower shelves is also complicated when there are differences in solid content of samples. According to Engelkemeir, et al⁽¹⁾, at 1.0 per cent solid angle, a 50 per cent difference in geometry was obtained between the value from UX with 10 mg of CeF_3 carrier and the value from UO_2 containing 27.0 mg/cm^2 . The values were 1.01 and 1.48 respectively.

Another possible error that might complicate measurement of various isotopes on the same instrument is that of varying the distance between counter and sample. Engelkemeir, et al⁽¹⁾, have found that, if activities of two different β -emitters, A_a and A_b , are measured for a series of geometries and the ratios A_a/A_b determined, it is found that these ratios are not constant. In some cases, going from 30 per cent to 2 per cent geometry, the ratio changes by as much as 40 per cent. Our measurements using Ra E and UX_2 also show a difference (Table 1).

Table 1: Change in the Ratio, RaE/UX_2 , with Varying Distance from the Counter Tube.

Shelf	Geometry	Increase in the Ratio from Shelf 2
2	0.10	---
3	0.05	2%
4	0.02	5%
5	0.01	14%

No attempt was made to determine the "true geometry" of the instruments used. The geometry with which we were concerned was an empirical one associated with the particular type of apparatus and mounting used throughout the program. By using exactly the same methods in calibration as were used in counting of experimental samples, many errors were minimized. In this manner, a high back-scattering error due to the use of porcelain capsules was cancelled to a large extent. Since geometry obtained using Ra E on shelf three was only 8 per cent higher than that obtained using UX_2 , the backscattering errors due to differences in the energy of the particles of the various isotopes were assumed to be small. Hence it is probable that differences in measurements of substances having maximum energies between those of Ra E and UX_2 (i.e. between 1.23 and 2.3 Mev) would be comparable under the same conditions of mounting and counting.

The major source of error in determining the absolute curie equivalents for solutions of beta ray emitters is in the correction for the absorption of beta particles by the air space between the sample and the counter and by the mica window of the counter. Since the shape of the early portion of a beta ray absorption curve is relatively uncertain, and since small differences in self-absorption and in the thickness of mica windows are less important the larger

the total absorption, it has been customary in this laboratory to make all measurements on the relatively straight portion of the absorption curve (usually under aluminum absorber of 50 mg/cm^2) and to make a straight line extrapolation to zero absorber. This method has given considerably more consistent results than that of extrapolating along the curve to zero absorber from a reading made without added absorbers.

As a final check on possible errors due to the back-scatter from porcelain capsules, samples of two of the most frequently used isotopes, I^{91} and Sr^{89} , were checked by mounting on mica and counting under the conditions used in the Chemistry Division. The values obtained for I^{91} with the aid of M. Freedman of the Chemistry Division agreed exactly with values obtained in the Biology Division, while those for Sr^{89} differed by less than 4 per cent. It is probable that the uncertainty in the absolute activity value is less than 10 per cent.

2.3 Absolute Standards. (a) U_3O_8 Standards: In the early attempts at counter calibration, known amounts of aged uranyl nitrate solutions were evaporated in large and small capsules and then placed in a furnace at 700°C until U_3O_8 was formed as an even layer on the capsules. The weight of U_3O_8 in the capsules was determined and the activity was measured. From the weight of the U_3O_8 , the absolute beta activity of the daughters in equilibrium with uranium could be determined. The ratio of the measured beta activity, corrected for absorption to the absolute activity, was the geometry of the counter.

The values obtained were later discarded because the high solid content rendered uncertain the corrections for scattering and absorption. However, the mounted preparations were retained for use as permanent reference standards (cf Section 2.4).

(b) UX₂ Standards. (1) Separation Methods: Two equally satisfactory methods of separation of UX from uranium were used.

Method A: Fifty milliliters of aged uranium solution containing 0.104 g of uranium per ml (and therefore, a UX₂ activity of 0.036 uc per ml) were evaporated to a small volume. The solution was transferred to a Lusteroid tube and 50 mg of La carrier were added. LaF₃ (and UX) was precipitated by adding a mixture of 10 ml of 6 N HF and 3 ml of 27 N HF. The zero time was recorded at this point. The precipitate was centrifuged down and washed twice with 6 N HF. To check the loss at this stage, the supernatants were collected in a platinum dish, fumed with HClO₄, and diluted to a known volume for measurement. The supernatants usually contained one or two per cent of the UX.

The washed precipitate was transferred to a glass centrifuge tube and stirred with concentrated NH₄OH to give a residue of La(OH)₃ (and UX). The residue was centrifuged and washed twice with 6N NH₄OH. The La(OH)₃ (and UX) was dissolved with HCl and made up to 50 ml in a volumetric flask. A number of standards were prepared in capsules using aliquots of this solution.

The Lusteroid tube used above was ashed, mounted, and counted. One or two per cent of the total activity usually remained in this residue.

The supernatants from the La(OH)₃ precipitation were collected and the La(OH)₃ precipitation was repeated after adding 10 mg of La carrier. This precipitate was washed twice with 6N NH₄OH and then dissolved with HCl. The solution was evaporated on a capsule and counted. Loss of activity here was about 1 per cent.

Method B: To 25 ml of an aqueous solution containing 0.104 g of uranium per ml, were added 25 mg of La carrier and 1.5 ml of 27 N HF. The resulting

LaF_3 and UX precipitate was centrifuged and washed twice with 10 ml of 6N HF. The supernatants were collected and carried through a second LaF_3 precipitation to check for losses.

Each precipitate was dissolved in a mixture of 8 parts HNO_3 and 1 part H_3BO_3 . The first solution was made up to 25 ml with 1 N HNO_3 and standard capsules were prepared using a number of aliquots. The entire second solution was mounted on a capsule and counted.

With either method essentially 100 per cent of the activity was accounted for.

(2) Determination of Geometry with UX₂ Standards: Since the absolute activity in the uranium solution and hence in the UX separated was known, it was necessary to count standards under absorbers of 50 mg per cm^2 to cut out UX₁, extrapolate to zero absorber on an absorption curve, correct to zero time, and divide the value obtained by the absolute activity to obtain the geometry.

(c) Ra E Standards. (1) Separation Method: One ml of a solution containing an equilibrium mixture of Ra D, E, and F with a radium E activity of about 27 uc was evaporated to dryness and then taken up with 10 ml of 0.1 N HCl. Twenty milligrams of powdered nickel were added. The mixture was heated to 80° C and was stirred for 2-3 minutes. It was then centrifuged and the Ni was washed three times with 0.1 N HCl. The powdered nickel containing Ra E and Ra F was dissolved with 0.5 to 1 ml of HNO_3 -HCl (aqua regia) and diluted to 10 ml. To the solution was added 20 mg of Bi carrier* and then an excess of NH_4OH was added. $\text{Bi}(\text{OH})_3$ precipitated and left Ni in solution as the NH_3 complex. Ra E (Bi^{210}) and Ra F (Po^{210}) were carried down on the precipitate. The $\text{Bi}(\text{OH})_3$ was dissolved with the smallest amount of HCl possible and was diluted to give

*In a preliminary trial the addition of Bi carrier was found necessary to get a separation of RaE from RaF.

an acidity of 0.1 N. This solution was passed through a column made up of 10 ml (wet) of 40-60 mesh IR-1 resin. The Bi and Ra F were adsorbed by the column. The Bi was eluted with 40 ml of 3N HNO₃ leaving the Ra F on the column. Five milliliter cuts were taken, and the zero time recorded. Aliquots of a central cut, which contained enough pure Ra E for all measurements, were mounted on a number of platinum discs for α counting, as well as in porcelain capsules for β counting.

(2) Determination of Geometry with Ra E Standards: The purity of the Ra E preparation was checked by obtaining absorption curves of Ra E, decay curves of Ra E, and growth curves of Ra F. The values for half-life and half-thickness checked the accepted values within the counting error of the instrument. Since the geometry of the α counter is known to be 52 per cent ⁽¹²⁾, the absolute Ra F α activity at any time, $I_p(t)$, can be determined. The absolute Ra E β activity at zero time, $I_E(0)$, can then be calculated from the equation:

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$$I_E(0) = \frac{I_p(t) (1 - \frac{\lambda_E}{\lambda_F})}{e^{-\lambda_E t} - e^{-\lambda_F t}} \quad (1)$$

The absolute Ra E β activity at any time, t , can be determined from the equation:

$$I_E(t) = I_E(0) e^{-\lambda_E t} \quad (2)$$

Since, in the early portion of the decay curve, the value of $I_p(t)$ is quite low, and in the late portion of the curve, the value of $I_E(t)$ becomes quite low, best results are obtained at about five days (the half-life of Ra E) when both activities are approximately 50 per cent of their maximum values.

The ratio of the activity measured on the beta counter at any time to the absolute beta activity at that time gives the geometry.

2.4 Preparation of Reference Standards: The U_3O_8 standards described in Section 2.3 (a) were used as reference standards. These capsules were counted through aluminum absorbers of 50 mg per cm² during the UX_2 and Ra E calibration, and factors were obtained for each U_3O_8 capsule using the geometry that had been determined by the UX_2 and Ra E at the same position. The U_3O_8 factors were obtained by using the following equation:

$$F = \frac{G^0}{M^0} \quad (3)$$

where G^0 represents the geometry determined with UX_2 or Ra E and M^0 is the activity of the U_3O_8 capsule as measured in counts per second.

Permanent standards were prepared with factors ranging from 0.000231 to 0.00084. The geometry can be determined at any time by measuring a reference standard at that time and multiplying the activity by the factor, F , of the standard measured.

2.5 Measurement of Unknown Solutions: An aliquot of the sample to be measured is dried in a capsule and its radioactivity measured. This value can be converted to curies per unit volume of solution by using the equation:

$$I = \frac{MA}{3.7 \times 10^{10} GV} \quad (4)$$

where I is the activity of the solution in curies/aliquot; M is the activity in the capsule as measured in counts per second; A is the correction to zero absorber; G is the geometry as determined with a reference standard; and V is the aliquot.

3. The Lauritsen Electroscope

A detailed description of the Lauritsen electroscope may be found in textbooks on nuclear physics. (2) It differs from the Geiger-Mueller counter in that it measures ionization rather than the number of disintegrations.

The electroscopes used in the Biological Research Section were calibrated in divisions per second per microcurie using the most linear portion of the electroscopes scale. The first calibration was based on a Sr^{89} sample of known activity obtained from Dr. J.G. Hamilton of Berkeley, California, and on the β -radiation of a known weight of uranium. On the basis of these calibrations, the electroscopes were also used for measurements of early Ba^{140} - La^{140} samples. Since the beta radiations from Ba^{140} - La^{140} in equilibrium do not differ greatly in energy from that of Sr^{89} , it was assumed that the relative sensitivities would be similar.

After the activities of the isotopes used had been accurately determined with Geiger-Mueller counters, the electroscopes were calibrated against these known activities. Values were obtained for Ux_2 , Sr^{89} , Na^{24} , Y^{91} , and P^{32} , and for Ba^{140} - La^{140} and Ce^{144} - Pr^{144} equilibrium mixtures. The values obtained on the various electroscopes were all of the order of one division per second per microcurie, and the range of sensitivities for the various isotopes on any one electroscopes fell within 0.5 d/s/uc. The sensitivity for Ba-La at equilibrium exceeded that for Sr^{89} by no more than 20 per cent.

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