[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF OREGON STATE COLLEGE]

A Gas-Sample Counting Method for Soft β-Emitters[1]

BY T. H. NORRIS

A simple, rapid and accurate gas counting method for soft β-emitters such as S^{35} and C^{14} is described. The method involves the use of a sample holder independent of the G-M counter.

In the course of work in this Laboratory with S^{35}-labeled sulfur dioxide, it has been convenient to develop a method for gas counting in order to avoid the labor of preparing solid counting specimens. The method, which would be equally applicable to C^{14} counting (say as carbon dioxide), appears to have certain original merits as compared with other reported[2,3] gas counting techniques for soft β-emitters and is therefore being reported here. Apart from its expeditiousness, gas counting is probably capable of yielding greater precision than solid-sample counting. As has been pointed out by Freedman and Hume[4] precision results cannot normally be obtained from the counting of β-emitters in solid form, because of irreproducibility of self-scattering and self-absorption effects; this is especially true of soft β-emitters such as C^{14} and S^{35}.

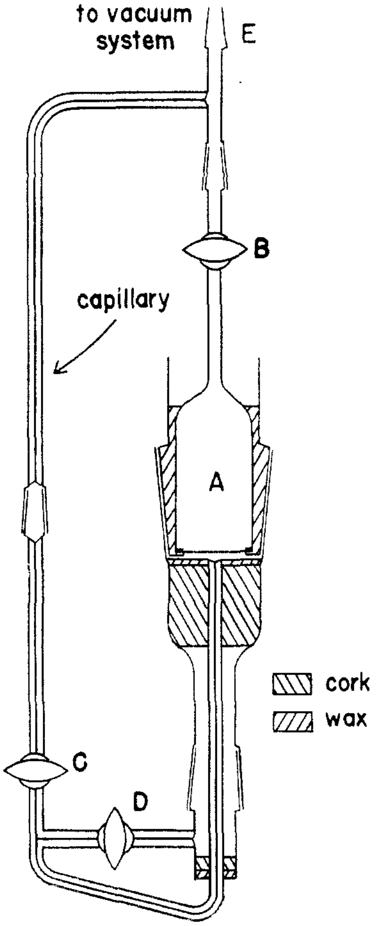

Fig. 1.—Gas sample holder filling assembly.

In previously reported[2,3] arrangements, the gas sample chamber has been permanently attached to a bell jar type counter, the mica window serving as a diaphragm between counting and sample gas volume. Evacuation and filling of the sample chamber thus leads to an undesirable flexing and straining of the window. In the present method this difficulty is avoided by making the gas holder an independent unit with its own window. Since the holder is filled in such manner as to avoid the production of any pressure differential, a much thinner window could be used than actually has been in the present instance; hence the net thickness of the two windows together might well not exceed that of a single window diaphragm as used in one of the above references.[3]

Apparatus.—The sample holder has been improvised from the cleaned glass shell of a discarded Tracerlab end window counter. This is provided at the top with an inlet tube and stopcock; a window (3.3 mg./cm.^{2}) is cemented to its end by means of Apiezon wax W. This holder in turn is placed within a #50/50 male ground joint, giving a snug fit, and waxed in place, the window being flush with the end of the joint.

Its volume being *ca.* 65 ml. the sample holder accommodates up to *ca.* 2.5 millimoles of sulfur dioxide. With the technique described below the smallest sample that is conveniently and accurately handled is *ca.* 0.06 millimole.

A female ground joint cover provides a pressure equalization chamber for the window during filling. Figure 1 shows the sample holder, A, assembled with cover and ready to be attached to the vacuum system. It may be seen that when a sample is put into the holder, a certain small portion goes into the "exterior" volume formed by the window cover; this, however, has been made negligibly small.

The apparatus could, of course, be simplified and its admittedly makeshift character much improved by appropriate glass-blowing and elimination of wax. A thinner window and a decrease in height of sample holder would be desirable.

Filling Technique.—For filling, the assembly shown in Fig. 1, attached to the vacuum system, is evacuated with stopcocks B and C open (D is for original evacuation of the volume it serves only). A sulfur dioxide sample to be counted, at any desired pressure up to an atmosphere, is then admitted. To minimize errors with small samples, it has been convenient to measure the pressure with the gas initially confined within a small known volume in the vacuum system. In no case was a pressure lower than 100 mm. actually read from a manometer; hence pressure measurement errors are considered negligible. After the sulfur dioxide, air is next admitted in amount sufficient to bring the pressure to exactly 740 mm. In these operations room temperature has been maintained at 27 ± 1°; corrections could, however, be applied as necessary for temperature variation.

After filling, B and C are closed and the gas not thus isolated is disposed of into the vacuum system prior to removal of the assembly at joint E. Then, in a hood, C is opened and the sample holder, A, removed from its cover. For counting, the sample holder is placed over an inverted end-window counter, the holder and counter windows being very close together. The counter (Tracerlab TGC-2, window 1.7 mg./cm.^{2}) is mounted within a female ground joint to ensure reproducible positioning of the holder.

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[1] Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 192, Department of Chemistry, School of Science.

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[3] F. Bonner and J. Turkevich, THIS JOURNAL, **73**, 561 (1951).

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Results.—Aliquots were taken from a supply of labeled sulfur dioxide for counting, at pressures ranging roughly from 18 mm. to 400 mm., giving activities from 600 to 11,000 c./m. The results, computed as counts per minute per millimeter of sulfur dioxide and normalized to give 100 c./m./mm. at zero pressure (actual values have been multiplied by 2.77), are plotted in Fig. 2. Each point represents an average of three determinations on separate samples, each determination being based on an average of at least three counts; total counting time was always sufficiently long to reduce the statistical error well below 1%. The observed standard deviations of the three sample averages for each point in Fig. 2 vary between 0.1% and 0.8%, mostly being $< 0.5\%$.

The apparent specific activity, as shown in Fig. 2, decreases slowly with increasing sample size because of increasing self-absorption resulting from the greater molecular weight of sulfur dioxide as compared with air. The *total* self-absorption within the air–sulfur dioxide mixture is not inconsiderable, the "thickness" of the gas sample ranging, for the data shown, between about 8.5 and 14 mg./cm.². For barium sulfate this would reduce the maximum specific activity to about 40%.

The self-consistency of the points in Fig. 2 represents a considerable improvement over the usual type of self-absorption curve data obtained on counting solid samples, where deviations of several per cent. from the smooth curve are not uncommon. The greatest deviation in Fig. 2 is less than 1%. To give an idea of the precision of the data, the smooth curve of Fig. 2 has been used to correct the actual experimental values to zero sample pressure. The corrected figures, given in Table I, show no divergence from the average as large as 1%.

TABLE I

CORRECTED SPECIFIC ACTIVITIES OF SULFUR DIOXIDE

Pressure SO_2, mm.	Spec. act. SO_2, corrected, c./m./mm.	Pressure SO_2, mm.	Spec. act. SO_2, corrected, c./m./mm.
18.0	36.1	101.7	36.2
33.5	36.1	105.7	36.3
52.1	36.0	189.3	36.0
70.4	36.3	293.3	36.2
86.3	36.0	393.3	36.0
		Average of all	36.1

Although it has been possible to obtain the present satisfactory results despite the makeshift character of the apparatus, the elimination of wax would probably yield a considerable improvement both in accuracy and convenience. With the samples as here used no significant memory effect was observed, yet material of a good deal higher specific activity does tend to leave a small residual and tenacious contamination. This difficulty is presumably attributable to the wax. In this regard it should be mentioned that, in the present case, background counts were always taken with the holder, empty of sulfur dioxide, in place above the counter tube. In this connection, too, it was shown that the holder, once filled, continues to give a steady counting rate over an extended period of time.

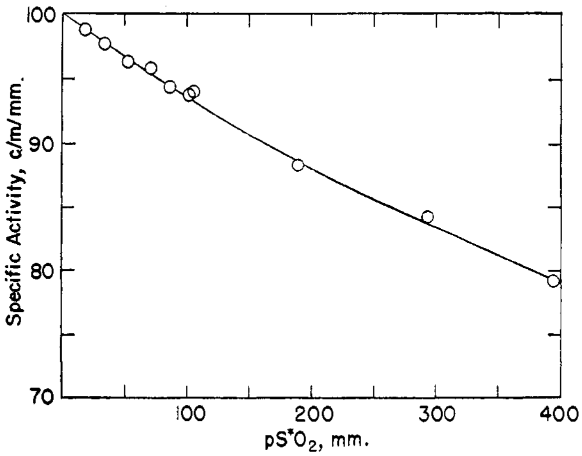

Fig. 2.—Apparent specific activity *vs.* sample size.

Sensitivity.—Since the use of air in addition to sulfur dioxide in the sample holder tends to decrease somewhat the sensitivity of the method, it is interesting to make a comparison with solid sample counting. Samples of the same labeled sulfur dioxide used above were converted to barium sulfate and counted[5] in conventional manner as thin layers on cupped planchets under and as close as possible to an end-window tube, correction being applied for a slightly lower counter sensitivity as compared with the first tube used. Then, applying the usual self-absorption curve for solid samples and Fig. 2 for gases, comparative activities to be expected for each method were calculated. Thus 0.194 millimole, a small sample, should give 56 mm. of sulfur dioxide in the holder, with 1.00×10^4 c./m./mmole, while on a planchet it should give 10 mg./cm.² of barium sulfate, showing 4.27×10^4 c./m./mmole; the gas method is 0.23 as sensitive as the solid method. On the other hand, 2.09 millimoles should give a gas pressure of 600 mm. and a solid thickness of 108 mg./cm.², with apparent respective specific activities of 7.26×10^3 and 4.58×10^3 c./m./mmole (the calculation involves an extrapolation of Fig. 2); sensitivity ratio is 1.59, favoring the gas technique. Thus, for sufficiently large samples, the latter is to be preferred.

It is to be noted that the sensitivity of the method could be increased almost twofold by use on the holder of a thinner window such as is commonly produced commercially on G–M tubes. For further increase in sensitivity, a decrease in the height of the holder, thus decreasing the amount of air used, would appear desirable. With the technique in its present status, a rough estimate indicates a counting efficiency of *ca.* 1%.

Finally it may be mentioned that, largely because of the favorable gas–solid molecular weight ratio, the gas method appears to offer the possibility of conveniently handling a greater range of sample sizes than solid-sample counting. Thus the figure given above, 108 mg./cm.², greatly exceeds infinite thickness for S^{35} and represents an excessive amount of material, whereas 600 mm. in the holder corresponds to a gas "thickness" of only *ca.* 17 mg./cm.².

(5) Thanks are due Mr. B. J. Masters of this Laboratory for assistance with these measurements.

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[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, MEHARRY MEDICAL COLLEGE]

Separation of the Radioisotopes of Silver and Palladium

BY GEORGE ROUSER[1] AND P. F. HAHN

A rapid quantitative method for the separation of small amounts of the isotope Ag^{111} from large quantities of palladium is described. Isotopes other than Pd^{111} are reported in the palladium fraction.

Pure palladium dissolves sparingly in concentrated nitric acid even after prolonged heating unless the material is finely powdered. Although a mixture of concentrated nitric and sulfuric acids will dissolve palladium slowly, a more rapid solution is preferable. The use of either of these methods may lead to the production of refractory palladium oxides if heating is not carefully controlled. The method to be described using aqua regia as solvent has been used with success[2,3] and is thus reported here in more detail.

The palladium was received as a 1-g. sheet after neutron bombardment in the Oak Ridge pile. Carrier silver nitrate (5–25 mg.) was added to a test-tube and allowed to coat the sides. The 1-g. palladium sample, containing an estimated 100 millicuries, was then added and treated with aqua regia with gentle heating for 1–2 minutes. Failure to add carrier before dissolving the sample resulted in varying losses depending upon the amount of carrier added (15% when 25 mg. of carrier was added). The acid suspension was then treated with concentrated ammonia and warmed until all of the material was in solution. The silver was reduced to the metal with an aqueous solution of ascorbic acid. The metallic silver was separated by centrifugation, washed with water and dissolved in nitric acid. After evaporation of the nitric acid solution to dryness, silver nitrate was dissolved in water. Complete removal of chloride and occluded palladium can be ensured by adding ammonia and reducing again with ascorbic acid, although this is generally not necessary.

The procedure up to the evaporation of the nitric acid solution requires as little as 30 minutes. The quantitativeness of the procedure was demonstrated by the failure to recover any appreciable amount of radio-silver after repeating the procedure a second time on the same palladium sample.

Attempts to separate the silver as the chloride resulted in lower yields and increased the operating time because of difficulties involved in removing the chloride. The material obtained as a chloride precipitate was also contaminated with palladium to a greater extent, as shown by following the decay curve of the sample.

When the radioactive decay of the sheets was followed with a Lauritsen electroscope, the presence of material with an apparent half-life of about 17 hours finally decaying to a stable 21-hour period was found. This apparent half-life of 17 hours has been observed by Seiler[4] to be due to the simultaneous decay of $Pd^{107,109}$ (half-life 13 hours) and Pd^{112} (half-life 21 hours). The final 21-hour period results from the decay of Pd^{112} after complete decay of $Pd^{107,109}$. Two days after removal from the pile 95% of the radioactivity was present in the palladium fraction. Since Pd^{111} (half-life 26 minutes), parent of Ag^{111} (half-life 7.5 days), had completely decayed at this time the activity was due to the two other palladium isotopes mentioned. Both of the latter isotopes of palladium decay to short lived silver isotopes and it is necessary to allow the silver fraction to stand overnight in order for them to decay and leave a pure sample of Ag^{111}.

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[1] Atomic Energy Fellow in the Biological Sciences. Present address: Department of Biochemistry, University of Rochester School of Medicine and Dentistry, Rochester, New York.

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