Rapid Determination of Strontium-90 in Tissue, Food, Biota, and Other Environmental Media by Tributyl Phosphate

Edmond J. Baratta and Thomas C. Reavey

In a rapid method for the determination of strontium-90 by tributyl phosphate extraction strontium-90 is determined by separation and analysis of its daughter product yttrium-90. The method is applicable to human tissue, food, biota, and other environmental media. For these types of samples, strontium-90 and its daughter, yttrium-90, are usually known to be in equilibrium. The method is sensitive to less than 1 pCi per sample of tissue or food ash. The samples are prepared by either dry- or wet-ashing techniques. The sample prepared for analysis is solubilized in nitric acid. The yttrium-90 daughter is extracted into equilibrated tributyl phosphate. The separated yttrium-90 is further purified by selective stripping and fluoride precipitation to remove the remaining contaminants which may have been carried over. Strontium-89 can also be determined in the same sample by precipitation of strontium prior to the yttrium-90 extraction.

Most methods for the determination of strontium-90 require a long ingrowth period, usually 10 days to 2 weeks (Butler 1963; Goldin *et al.*, 1959; Peppard *et al.*, 1957) after purification of the strontium. Some require that the strontium-90, yttrium-90 reach equilibrium after separation of the strontium fraction with the resultant corrections for strontium-89 (Porter *et al.*, 1967). Other procedures are applicable to only a specific medium (Baratta and Ferri, 1967; Eisenbud and Petrow, 1964; and Velten and Goldin, 1961). This paper presents a rapid method for the determination of strontium-90 by tributyl phosphate extraction of the yttrium-90 daughters. The method is applicable to a variety of sample types such as human tissue, food, biota, and other environmental media where strontium-90 and its daughter, yttrium-90, are usually known to be in equilibrium. The method is sensitive to less than 1 pCi per gram of food ash and less than 1 pCi per sample of tissue. It is fairly rapid, requiring under 4.0 man-hours for the analysis of four samples. The strontium fraction may be remilked if necessary.

The yttrium-90 is separated directly from the ash solution and measured in a low background beta counter. Samples are prepared either by dry- or wet-ashing techniques. The sample for analysis is solubilized in nitric acid. The yttrium-90 daughter is extracted into equilibrated tributyl phosphate. The separated yttrium-90 is further purified by selective stripping from the tributyl phosphate and a rare earth fluoride precipitation to remove the remaining contaminants which may have been carried over. The yttrium-90 is precipitated as the oxalate and (2.26 MeV maximum beta energy) counted in a low background beta counter. Yield is determined by converting the oxalate to the oxide.

Strontium-89 can be determined also in the same sample by precipitation of the strontium prior to the yttrium-90 extraction. The strontium fraction is purified and counted in a low background beta counter.

EXPERIMENTAL

Figure 1 shows the flow of analysis used in the determination of strontium-90 and strontium-89 by tributyl phosphate.

U. S. Department of Health, Education, and Welfare, Consumer Protection and Environmental Health Service, Environmental Control Administration, Bureau of Radiological Health, Northeastern Radiological Health Laboratory, 109 Holton Street, Winchester, Mass. 01890

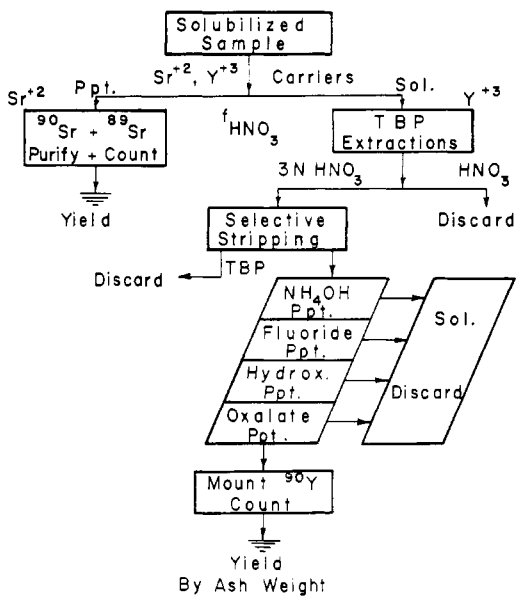

Figure 1. Flow of analysis

Apparatus. A low level background beta counter with a background of less than one count per minute was used.

Procedure. 1. Grind to a fine powder a weighed portion (about 15 grams) of food ash or other ashed media. Transfer to a 125-ml. beaker, and add 70 ml. of concentrated nitric acid. *Use Hood.* When reaction has subsided, stir and place on a hot plate. Heat with occasional stirring until brown fumes disappear. Add 30 ml. of H_2O. Heat and stir for a few minutes.

2. Filter through a 5.5-cm. glass filter paper into a 150-ml. suction flask. When wetting the filter paper, make sure no water enters flask. This prevents dilution of the acid.

3. Transfer filtrate to a 400-ml. beaker adding 1 ml. each of Sr^{2+} and Y^{3+} carriers (90 and 20 mg. per ml., respectively). Add 130 ml. of fuming (yellow) HNO_3, using a portion to rinse out suction flask. Place beaker in an ice bath for at least 15 minutes. Note the time, the start of yttrium-90 decay.

4. Transfer mixture to a 250-ml. centrifuge bottle and centrifuge for 20 minutes. (Speed 2000 r.p.m.)

5. Place supernate in a 500-ml. separatory funnel and add 30 ml. of H_2O. (If a strontium-89 determination is to be

Table I. Comparison of TBP *vs.* Nitric Acid Separation Methods

Bread Ash Pool Sample, pCi ^{90}Sr per Gram Ash		Diet Food Sample, pCi ^{90}Sr per Gram Ash	
TBP method	Nitric acid method	TBP method	Nitric acid method
1.23	1.26	1.0	1.1
1.27	1.37	0.52	0.58
1.54	1.27	0.89	0.87
1.43 mean ± σ	1.35 mean ± σ	0.85	0.87
1.24 1.23 ± 0.15	1.08 1.25 ± 0.10	0.75	0.73
1.10	1.16	0.72	0.68
1.06	1.36	1.36	1.3
1.12	1.35		
1.19	1.21		
1.12	1.15		
$\bar{d}$ = −0.026		$\bar{d}$ = −0.0057	
s_d = 0.1689		s_d = 0.0574	
n_d = 10		n_d = 7	
t = 0.154		t = 0.263	
Critical value of t at 95% C.L. = 2.262		Critical value of t at 95% C.L. = 2.447	

made, save the nitrate precipitate.) Add 50 ml. of freshly equilibrated TBP to the separatory funnel and shake for 3 to 4 minutes. Transfer the aqueous phase to a clean 250-ml. separatory funnel. (To equilibrate TBP, shake TBP twice with an equal volume of 14*N* HNO_3 for 5 minutes. Discard the aqueous phase.)

6. Add another 50 ml. of the TBP and shake for 3 to 4 minutes. Discard the aqueous phase.

7. Combine the organic phases from steps 6 and 5 in the 250-ml. separatory funnel. Wash the empty funnel with 40 ml. of 14*N* HNO_3 and add it to the 250-ml. funnel containing the organic phase. Shake for 2 to 3 minutes. Discard the aqueous phase.

8. Add 40 ml. of 14*N* HNO_3 to the organic phase. Shake for 2 to 3 minutes. Discard the aqueous phase. Repeat.

9. Add 50 ml. of H_2O to the separatory funnel and shake for 2 to 3 minutes. Transfer the aqueous phase to a 400-ml. beaker. Repeat twice.

10. Add 25 ml. of 3*N* HNO_3 to the separatory funnel, and shake for 2 to 3 minutes. Combine the aqueous phase with that from step 9. Repeat twice.

11. Dilute solution in the 400-ml. beaker using 5 to 10 ml. of distilled H_2O and add concentrated NH_4OH until a brownish precipitate forms. Transfer solution and precipitate to a 250-ml. centrifuge bottle and centrifuge. (When bone ash is used, a white precipitate appears; proceed to step 15.)

12. Carefully decant supernate (discard). Transfer precipitate using H_2O into a plastic (polypropylene or polycarbonate types) centrifuge tube. Centrifuge and discard supernate.

13. Dissolve the precipitate in 2 ml. of concentrated HCl. Dilute to 30 ml. with H_2O and add 2 ml. of 48% HF solution. Centrifuge and discard supernate.

14. Dissolve the precipitate in 2 ml. of saturated H_3BO_3 solution and 2 ml. of concentrated HCl. When dissolved, dilute to about 20 ml. with H_2O. Add concentrated NH_4OH until the solution is alkaline. Centrifuge and discard supernate.

15. Dissolve precipitate in about 2 ml. of concentrated HCl. Transfer carefully to a 40-ml. glass centrifuge tube using not more than 20 ml. of H_2O. Add 10 ml. of 2*N* oxalic acid, adjust the pH to 1.0 to 1.5 using concentrated NH_4OH, and heat on a water bath for about 20 minutes. Centrifuge and discard supernate.

16. Place a 2.4-cm. Whatman No. 542 filter paper on a filtration apparatus. Take up the precipitate in 10 ml. of warm H_2O and transfer to the filter paper using warm H_2O. Wash the precipitate with three 10-ml. portions of absolute ethyl alcohol. Continue suction until the alcohol has been removed from precipitate.

17. Remove the filter paper from the apparatus and dry in an oven at 125° C. for about 20 minutes. Cool to room temperature, mount on a nylon holder, cover with mylar, and count for the β^- activity of yttrium-90 in a low background beta counter. Record the time of counting to determine the decay factor of yttrium-90 from the time of separation to the counting time.

18. After counting, carefully disassemble the sample holder, transferring the filter paper and the mylar to a preweighed platinum crucible. Ignite at 800° C. for 1 hour. Cool to room temperature, re-weigh the crucible, and determine the chemical yield.

The strontium-90 activity is computed as follows:

$$^{90}Sr, \text{ pCi/per gram ash} = \frac{\text{gross c.p.m.} - A - B}{2.22\ (C)\ (D)\ (E)\ (W)}$$

Where A = detector background; B = reagent blank; C = chemical yield; D = detector geometry; E = decay factor for yttrium between separation and counting; W = weight of ash in grams.

Note: Weight of sample used when wet ashed.

RESULTS AND DISCUSSION

Previous studies (Public Health Service, 1967) have confirmed the purity of the yttrium-90. The over-all yield for the yttrium carrier has averaged 80% based on multiple analyses for various media (bone, tissue, food, and vegetation).

The method was compared with the previously used nitrate precipitation procedure (Public Health Service, 1967) using a bread ash pool sample and with a total diet food sample. Results are in Table I. The method was also compared with simulated spiked bone samples at three different levels (Table II). These three types of ashed samples represent a wide range of environmental media: The bread ash, a specific media, the diet food, containing a wide matrix of material and bone, a sample containing large amounts of calcium.

Table II. Simulated Bone Ash Sample

Known, pCi ^{90}Sr per Gram Ash	Determined,[a] pCi ^{90}Sr per Gram Ash[b]
0.99	0.93 ± 0.13
2.97	2.71 ± 0.24
9.90	9.90 ± 1.81

[a] Average of three replicate determinations. [b] Mean at ±2 SD.

Table III. Decontamination Factors

Cerium-144	$>2 \times 10^3$
Iron-55	$>3 \times 10^3$
Zinc-65	$>2 \times 10^3$
Zirconium-Niobium-95	$>5 \times 10^2$
Manganese-55	$>10^3$
Strontium-90	$>4 \times 10^3$
Ruthenium-106	$>2 \times 10^3$
Cobalt-60	$>10^3$
Thorium-230	$>2 \times 10^3$
Uranium-238	$>10^3$
Promethium-147	$>2 \times 10^3$
Radium-226	$>5 \times 10^2$
Lead-210	$>10^3$
Actinium-227	$>4 \times 10^3$
Barium-140	$>10^3$
Lanthanum-140	$>10^3$

The decontamination factors for the various naturally occurring nuclides, fission, and activation products are presented in Table III. These nuclides represent those normally found in diet foods, human bone, and tissue and vegetation samples. The decontamination for the naturally occurring radionuclides was more than adequate for the amounts normally found in the media analyzed. The radionuclides from fission and activation products were satisfactory for human bone, diet food, human tissue, and vegetation.

Reagent blanks were determined and did not contain any appreciable activity above background. Depending upon the type of counter used, the background did not increase appreciably using the nylon ring and disk with glass filter paper covered with mylar or the Millipore type filter paper. The average increase was less than 9% with a counter having a background of 0.44 c.p.m. and less than 5% for a counter with a background of 1.0 c.p.m. These minor increases are taken into consideration in the calculations.

Precision. The precision was compared with the previously used procedure (Public Health Service, 1967), using the data from the analysis of a bread ash pool sample. The standard deviation of ±0.15 pCi per gram of ash for the TBP method is not significantly different from ±0.10 pCi per gram of ash for the previous method. The over-all standard deviation of the method, as determined by measurement of seven sets of food samples is ±0.061 pCi per gram of ash. This means that for the measurement of strontium-90 for diet samples having a concentration of about 1 pCi ^{90}Sr per gram ash, the standard deviation of a single determination is about ±0.061 pCi per gram ash, Table I. The one sigma error for a human bone sample on 43 sets of duplicates had been found to be ±0.105 pCi ^{90}Sr per gram ash. For human tissue, the error was comparable. The error for vegetation was similar to that for diet.

Accuracy. The accuracy of the method was determined by comparing the results of seven food samples and ten bread ash samples run by both methods. Student's "t" test was used to determine if any significant difference in accuracy exists between the two methods. The results are shown in Table I.

$\bar{d}$ = average difference between results of the two methods.
s_d = standard deviation of the differences.
n_d = number of differences.

Since the calculated value for "t" for both types of samples is less than the critical value, there is no significant difference in accuracy between the two methods.

ACKNOWLEDGMENT

The authors acknowledge the valuable assistance of Ella Peers in this study.

LITERATURE CITED

Baratta, E. J., Ferri, E. S., *Anal. Chem.* **39,** 846 (1967).
Butler, F. E., *Anal. Chem.* **35,** 2069 (1963).
Eisenbud, M., Petrow, H. G., *U. S. At. Energy Comm. Rt.* **AT-(30-1)** 2896 (1964).
Goldin, A. S., Velton, R. J., Frishkorn, G. W., *Anal. Chem.* **31,** 1490–2 (1959).
Peppard, D. G., Mason, G. W., Moline, S. W., *J. Inorg. Nucl. Chem.* **5,** 141 (1957).
Porter, C. R., *et al., Environ. Sci. Technol.* **1,** 745 (1967).
Public Health Service, "Radioassay Procedures for Environmental Samples," Department of Health, Education, and Welfare, PHS Publication No. 999-RH-27 (1967).
Velten, R. J., Goldin, A. S., *Anal. Chem.* **33,** 128 (1961).

Received for review March 27, 1969. Accepted August 11, 1969.