*An Ion Exchange Method for the Determination of Cesium-137 and Strontium-90 in Fallout**

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Several methods for the determination of cesium-137 and strontium-90 in fallout deposits have been reported,[1-6] some of them including ion-exchange techniques. The main aim of the radiochemical analysis of fallout has been the determination of cesium-137 and strontium-90, the most important radionuclides among the fission products because of their long half-lives. It is, therefore, necessary to develop a more rapid and less tedious method for these important radionuclides than the conventional ones.

The methed reported here for the determination of cesium-137 and strontium-90 from the same sample is based on three previous studies by the the present author and his coworker. The first work dealt with the phenomena of the hydrolysis of metal ions adsorbed on cation exchange resin.[7] The second described the ion-exchange separation of a small quantity of strontium from a large quantity of calcium.[8] The third presented fundamental data for the specific adsorption of cesium by a phenol-sulfonic acid type cation-exchange resin.[9]

Experimental

Chemicals. — *Cation Exchange Column A.* — H^+-form of Amberlite CG-120 (sulfonic-acid type cation exchange resin), 100∼200 mesh, 2.0×15 cm. column.

Cation Exchange Column B.—Diaion BK (phenol-sulfonic-acid type cation exchange resin), 100∼120 mesh, equilibrated with "solution II," 1.0×4 cm. column.

Elutriant I. — 1 : 1 mixture of a 2 M ammonium acetate solution and methanol.

Elutriant II.—2 M ammonium acetate solution.

Solution I.—A mixture of a 5 M ammonium formate solution and 5 M aqueous ammonia in the ratio of 1 : 40 (pH 11.3).

Solution II.—A tenfold diluted solution of solution I (pH 11.0).

All chemicals used were of reagent grade.

Radioactivity Measurement. — Gamma-activity was measured by a scintillation counter with a single-channel pulse height analyzer, and the β-activity by an anti-coincidence low-background Geiger-Muller counter.

Procedure.—As a result of extensive studies of the analytical procedure, the following method was established for the analysis of monthly fallout deposits collected on a 50×50 cm. tray.

An extract of the fallout deposit with 6 N hydrochloric acid was subjected to analysis after organic matter had been decomposed with nitric acid and after silica had been removed by a conventional procedure. The extract was evaporated to dryness, and then the residue was dissolved in 5∼10 ml. of 3 N hydrochloric acid and diluted with water to 30∼50 ml. The solution was passed through column A and the column was washed with 50 ml. of water. Then, 300 ml. of elutriant I was passed through the column at the flow rate of 2∼3 ml./min. Sodium, potassium, magnesium and calcium were eluted in this portion. In the next step, cesium and strontium were eluted with 225 ml. of elutriant II. The effluent was evaporated to dryness on a water bath, and the residue was heated under an infrared lamp; thus the ammonium formate in the residue could be sublimed.

Two milliliters of solution I and 10 ml. of water were added to the vessel to dissolve the residue. The total strontium content of the solution was determined by titration with a 0.01 M EDTA standard solution adding 1 ml. of a 0.01 M magnesium-EDTA solution, and Eriochrome Black T as an indicator. After the titration, a volume of EDTA nearly equal to the titre was further added, and the solution was diluted to 20 ml. with water. The solution was poured into column B. The column was washed with 20 ml. of a mixture of 2 ml. of solution I, a volume of EDTA equal to the titre, and water.

Strontium-90 activity in the effluent was determined with a low-background Geiger-Muller counter by the usual yttrium-milking method after the EDTA had been decomposed with nitric acid and hydrogen peroxide. The γ-activity of the cesium-137 remaining in the column was measured with

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* The manual form of the procedure reported here was included in an article in *Japan Analyst* (*Bunseki Kagaku*), **9**, 787 (1960).

1) F. J. Bryant, A. C. Chamberlain, A. Morgan and G. S. Spicer, AERE. HP: R-2353 (1957).

2) Radiation Council, Japan Atomic Energy Commission, "Methods of Analysis for Strontium-90" (1960), "Methods of Analysis for Cesium-137" (1962), Science and Technology Agency, Japanese Government (In Japanese).

3) Health and Safety Laboratory, HASL manual standard procedures, with revision and modifications in August 1959. NYO-4700 (1960).

4) T. T. Sugihara, H. I. James, E. J. Troianello and V. T. Bowen, *Anal. Chem.*, **31**, 44 (1959).

5) T. Sotobayashi and S. Koyama, *J. Faculty of Sciences, Niigata Univ., Ser. I*, 3, No. 2, 103 (1962).

6) H. Tsubota, *Japan Analyst* (*Bunseki Kagaku*), **9**, 783 (1960).

7) H. Tsubota and H. Kakihana, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1650 (1961).

8) H. Tsubota, This Bulletin, to be published.

9) H. Tsubota, ibid, **36**, 1038 (1963).

a scintillation counter, by taking the resin out from the column into a suitable vessel with water and by drying under an infrared lamp. Alternatively, cesium-137 was eluted from the column with 30 ml. of a 1 : 1 mixture of 1 M formic acid and a 1 M ammonium formate solution. The effluent was evaporated to dryness, and the residue was sublimed under an infrared lamp. The vessel was rinsed thoroughly with 5 ml. of a 1 : 1 mixture of 1 M formic acid and 1 M ammonium formate to dissolve the cesium. The solution was transferred to a stainless steel counting dish and again evaporated to dryness under an infrared lamp to expel the ammonium formate completely. The β-activity of cesium-137 in the dish was measured with a low-background Geiger-Muller counter.

Examination of the Procedure

To check the efficiency of separation, an artificial solution with a composition similar to the extract of fallout was used. Its composition is shown in Table I.

TABLE I. CHEMICAL COMPOSITION OF ARTIFICIAL FALLOUT SAMPLE

Metal ion	Content, mg.
Na^+	200
K^+	50
Mg^{2+}	50
Ca^{2+}	120
Fe^{3+}	80
Al^{3+}	40

Total : About 1.5 g. as chlorides (ca. 30 meq.)

The Behavior of Metal Ions which Tend to be Hydrolyzed.—The artificial fallout solution containing cerium and zirconium labeled with cerium-144 and zirconium-95 was passed through column A. The column was treated with elutriants I and II by the procedure mentioned above, and the effluent was divided into 10 ml. fractions. The radioactivity measurement of cerium and zirconium and the colorimetrical determination of ferric and aluminum ions were carried out in each fraction. Very small amounts of these metal ions were sometimes detected in the fraction collected before the calcium fractions but not in other fractions. It was thus verified that metal ions which tend to be hydrolyzed are not eluted from the cation exchange column with elutriant I (containg methanol), a finding which is in accordance with the former findings with aqueous elutriants.7)

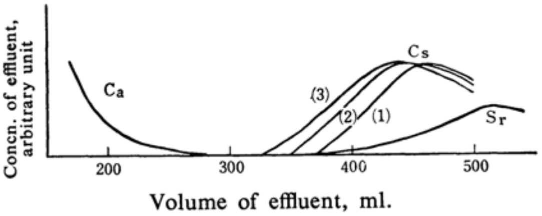

Fig. 1. Separation of cesium from calcium.

Column : Amberlite CG-120, 2.0 $\phi\times$15 cm.
Sample : Artificial fallout solution containing cesium and 10 mg. of strontium
Elutriant : 1 : 1 mixture of 2 M ammonium acetate aqueous solution and methanol
Curve (1) : Amount of cesium is 0 mg. (carrier-free Cs-137).
Curve (2) : Amount of cesium is 5 mg.
Curve (3) : Amount of cesium is 10 mg.

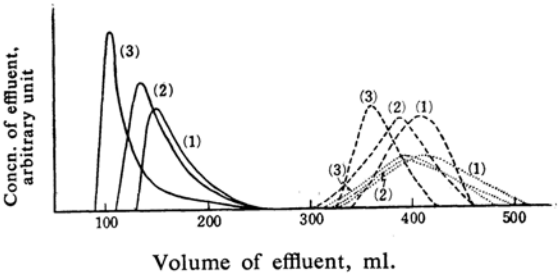

Fig. 2. Elution curves of calcium, strontium and cesium.

Column : Amberlite CG-120, 2.0 $\phi\times$15 cm.
Sample : Artificial fallout solution containing 10 mg. of cesium and 20 mg. strontium. Amounts of calcium were varied; curve 1, 120 mg.; curve 2, 180 mg.; and curve 3, 240 mg.
Elutriant : 300 ml. of elutriant I and 230 ml. of elutriant II.
—— : Elution curves of calcium
…… : Elution curves of strontium
- - - : Elution curves of cesium

The Elution of Strontium and Cesium from Column A.—Figures 1 and 2 show the elution curves from column A for artificial fallout solutions containing varying amounts of cesium labeled with cesium-137 and for those containing various amounts of calcium. The elutriants used are specified along each curve in the figures. From the figures, it is evident that strontium is eluted together with cesium and that both ions are eluted later than and are well separated from calcium. The effect of the change in calcium concentration, as actually encountered in the fallout, can also be shown. The increasing calcium concentration makes the separation more complete. These findings are in agreement with the former findings.8)

The Capacity of Column A.—The column dimensions were decided upon by assuming that the maximum dimensions would be required if all the cations in the artificial solution were to be replaced by calcium. By using a column 15 cm. long and 2 cm. in diameter, fallout extract, the cation content of which is equivalent to at least 30 meq., would be treated. A sample of greater cation content than that

TABLE II. ADSORPTION OF STRONTIUM ON A COLUMN OF PHENOL-SULFONIC ACID TYPE CATION EXCHANGE RESIN[*1]

		Radioactivity found[*4]			
		In the effluent of			In the column %
Sample solution[*2]	Radioactive tracers added	Sample solution %	Washing solution[*3]		
			0~25 ml., %	25~50 ml., %	
A	Sr-89	27.0	2.1	0.0	68.5
A	Sr-90+Y-90	24.6	2.1	0.0	70.8
B	Sr-89	97.6	3.3	0.1	0.7
C	Sr-89	95.5	4.5	0.0	0.04
C	Sr-90+Y-90	82.0	20.8	0.0	0.02
C	Cs-137	0.0	0.0	0.0	99.1

[*1] $1.0\,\phi\times4$ cm. column.

[*2] 50 ml. of solution II, containing 10 mg. (0.11 mmol.) of Sr carrier, and EDTA (A) 0, (B) 0.11 mmol. and (C) 0.22 mmol. respectively.

[*3] Solution II containing EDTA (A) 0, (B) 0.11 mmol. and (C) 0.11 mmol. respectively.

[*4] Added radioactivity was taken as 100%.

of the artificial solution can be treated by a larger column. The length of the column (L cm.) necessary to treat W g. (as chlorides) of a sample is given by:[8]

$$L=10+5\frac{W}{1.5}$$

and the volume of elutriant (V ml.) by:

$$V=V_0\frac{L}{15}$$

where V_0 is the volume of elutriant required when the value of W is 1.5. Actually, 2 g. of chlorides can be treated with a column 15 cm. long, as will be shown later in Table III. Hence, L calculated in this manner has reasonable allowance.

The Separation of Cesium and Strontium with Column B.—Cesium is adsorbed on a phenol-sulfonic-acid type cation exchange resin from an ammoniacal solution.[9] When solution II containing strontium labeled with radioactive strontium was passed through column B and the column was washed with solution II, a considerable amount of strontium remained in the column, as is shown in Table II. When EDTA was added to the sample solution and washing solution, however, no strontium (nor yttrium) remained. Even when twice as much EDTA as strontium was added to solution II, cesium was not eluted until 150 ml. of the washing solution had passed.

The cesium adsorbed on the resin could not be eluted with water, and was eluted very slowly with a neutral solution of sodium or ammonium salt, but it was eluted easily and completely with acidic solutions. Elution curves for cesium from column B with different elutriants are shown in Fig. 3. The elution curve with 0.5 N hydrochloric acid consists of two parts, a high peak probably due to elution from the phenolic group, the tailing part probably due to elution from the sulfonic group. Elution curves with concentrated acids, such as 3 N hydrochloric acid or a 2 M formate buffer solution, had a typical form of favorable elution.

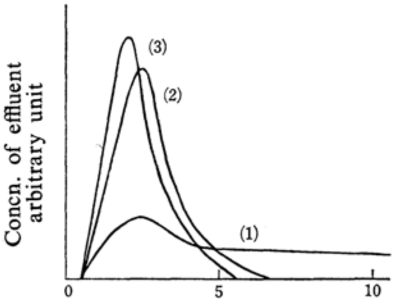

Fig. 3. Elution curves of cesium from a column of phenol-sulfonic acid type cation exchange resin.
Column: Diaion BK, $1.0\,\phi\times4$ cm.
Elutriant: (1) 0.5 N HCl
Elutriant: (2) 3 N HCl
Elutriant: (3) 1 : 1 mixture of 2 M formic acid and 2 M ammonium formate.

Results

The analysis was carried out by using an artificial fallout solution containing labeled strontium and cesium. The results are shown in Table III. The recovery was 98±4% for strontium and 99±3% for cesium.

The results of analyses of monthly fallout deposits are shown Table IV. In this case, samples were collected on the roof of the

TABLE III. RECOVERY OF STRONTIUM AND CESIUM*1

Radioactive and non-active cations added to the artificial solution				Radioactive and non-active cations found		
Ca*2 mg.	Sr*3 mg.	Cs mg.	Radioactive nuclide*4	Sr mg.	Sr-90 %	Cs-137 %
80	10.2	10.0	Sr-90	10.1_5	93.7	—
80	10.2	10.0	Cs-137	10.0_3	—	99.0
80	0.30	10.0	Sr-90, Cs-137	0.32	99.3	102.9
80	1.20	1.00	Sr-90, Cs-137	1.15	102.1	95.6
0	1.12	1.00	F. P. (less Sr-90, Cs-137)*5	—	(20.1 c.p.m.)	
0	10.2	1.00	Sr-90, Cs-137	8.40	79.7	56.3
0	10.2	1.00	Sr-90, Cs-137	9.90	98.2	97.1

*1 Column length is 15 cm. for each run except for the last run (20 cm.). Amount of the artificial solution corresponds to 1.5 g. of chlorides for first 5 runs and 3.0 g. for last 2 runs.

*2 Amount of calcium added to the artificial solution, which contains 120 mg. of calcium.

*3 Including the strontium in the calcium salt as an impurity.

*4 Radioactivity added were:
Sr-90: 43.4×10^3 c.p.m.
Cs-137: 6.7×10^3 c.p.m.

*5 Mixture of fission products (cooled for 3 months) from which Sr-90 and Cs-137 were removed. Total radioactivity added was about 5×10^5 c.p.m.

TABLE IV. RESULTS OF RADIOCHEMICAL ANALYSES OF CESIUM-137 AND STRONTIUM-90 IN MONTHLY FALLOUT DEPOSITS

Collected in	Present method		Precipitation method	
	Cs-137 mc./km^2	Sr-90 mc./km^2	Cs-137 mc./km^2	Sr-90 mc./km^2
May 1959	3.93	1.91	4.10	1.86
June	2.32	0.78	2.60	0.78
July	0.98	0.17	0.84	0.17
Aug.	0.44	0.13	0.29	0.14
Sept.	0.54	0.09	0.29	0.09
Oct.	0.47	0.04	0.21	0.03
Nov.	0.28	0.03	0.32	0.04
Dec.	0.17	0.08	0.18	0.09
Jan. 1960	0.19	0.08	0.18	0.07

National Institute of Health in Tokyo, Japan, and the hydrochloric acid extracts of the sample were divided into two portions, one being analyzed by the present method and the other by the usual fuming acid-tungstosilicate-perchlorate method.[2] The agreement between the results of these two methods was satisfactory as a whole.

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