Separation of Radioactive Cesium in Biological Materials

By Noboru YAMAGATA and Toshiko YAMAGATA

(Received July 15, 1958)

A number of procedures for the separation of low concentrations of radioactive cesium in natural materials have been studied by several workers. When the final radioassay is to be achieved by beta counting, the first problem is the decontamination of natural radioactive elements, rubidium and potassium, the second is the removal of the other fission activities, particularly of the long-lived strontium-90 and cerium-144, and the third is the method of elimination of the bulk of other elements including sodium and potassium.

In the earlier work on the determination of cesium-137 in biological materials[1], the authors adopted the usual method of separation of the alkali elements, that consists in the elimination of the sulfate ion with barium chloride followed by the removal of alkaline earth elements as carbonate and oxalate. Those procedures were supposed to carry down other fission activities, although the loss of cesium in the whole process was proved to be very small as already reported[2]. The bulk of the sodium chloride and a part of the potassium chloride were removed by hydrochloric acid—the ethanol method and the elimination of rubidium and potassium were effectively undertaken by the cesium chloroplatinate precipitation method in an aqueous medium[3].

This method is certainly generally useful and suitable but the first half of the procedure is troublesome when dealing with a large number of samples. The present study deals with the examination of the direct precipitation of cesium with ammonium phosphomolybdate and a simple and rapid separation method for cesium-137 is presented.

Principle.—The method is based on two separations involving the selective precipitation of cesium with ammonium phosphomolybdate in an acid medium and the relative solubilities of the alkali chloroplatinates in water.

Because an excess of phosphate ion which is usually present in the processed solution of food, urine or tissues will interfere with the perfect precipitation of cesium with ammonium phosphomolybdate, it must be previously removed by alkalination to form calcium and magnesium phosphates. In this procedure a partial elimination of other fission activities can be attained. The precipitated cesium ammonium phosphomolybdate is dissolved in ammonium hydroxide and after boiling to expel excess of ammonia, the precipitation with chloroplatinic acid is performed. The precipitate is weighed and mounted for beta counting.

Experimental

Special Reagents. — Ammonium molybdate solution, 10% of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water; Cesium carrier (CsCl), 10mg. of Cs per ml. of water; Chloroplatinic acid, 10% of $H_2PtCl_6\cdot 6H_2O$ in water; Salt solutions, containing 20 g. of K^+,

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[1] N. Yamagata and T. Yamagata, *Japan Analyst* (*Bunseki Kagaku*), **7**, 433 (1958).

[2] N. Yamagata and T. Yamagata, ibid., **5**, 37 (1956).

[3] N. Yamagata and E. Tajima, This Bulletin, **30**, 674 (1957).

Na^+, and Ca^{2+} respectively, 10 g. of Mg^{2+} and 0.2 g. of Fe^{3+} per liter of water.

Radioactive tracers. — ^{137}Cs (carrier-free), Nitrate in nitric acid solution, from the Radiochemical Center, England; ^{89}Sr (carrier-free), Chloride in hydrochloric acid solution from Oak Ridge National Laboratory Batch No. 229A; ^{144}Ce (carrier-free), Nitrate in nitric acid solution from Oak Ridge National Laboratory Batch No. 50; ^{91}Y (carrier-free), Chloride in hydrochloric acid solution from Oak Ridge National Laboratory Batch No. 76.

To make the conditions of precipitation as close as possible to the actual case, a salt solution containing potassium, sodium, calcium, magnesium and ferric ions was prepared. It was considered to possess a similar elementary composition to food, urine or tissues. A proper quantity of the salt solution was used for the tracer experiments.

Conditions of phosphomolybdate precipitation. — As for the conditions of phosphomolybdate precipitation, above all, for interfering substances, the temperature and the composition of precipitate, many investigations have been reported. As far as only the recovery of cesium is concerned, it matters but little what the composition of the phosphomolybdate precipitate may be. For this reason, the solution containing the phosphate ion was heated to 50～60°C and then ammonium molybdate solution was added. To determine the minimum volume of ammonium molybdate solution necessary to precipitate cesium completely, an experiment was performed of which the results are shown in Table I. Provided that one mole of P_2O_5 combines with 24 moles of MoO_3, 0.68 ml of 10% ammonium molybdate solution is equivalent to 1 mg. of phosphorus. The result of the experiment indicates that about three times or more excess of the reagent solution is needed for the perfect precipitation of cesium.

TABLE I

PRECIPITATION OF CESIUM WITH AMMONIUM PHOSPHOMOLYBDATE

Total volume of soln., 50 ml.; conc. HNO_3, 2 ml.; H_3PO_4 (as P), 1 mg.; Cs carrier, 2 mg.

Soln.		NH_4 molybdate soln. added (ml.)	Cs pptd. (%)
Salt soln.	5 ml.	0.5	0
〃	〃	1.0	3.6
〃	〃	2.0	96.9
〃	〃	3.0	100.1
〃	〃	5.0	99.6
Oak leaf ash (processed)	2 g.	3.0	98.8
Human urine (processed)	50 ml.	3.0	95.7
Bittern	10 ml.	3.0	99.6
〃	30 ml.	3.0	95.9
〃	42 ml.	3.0	85.6

Several samples of natural materials were substituted for the salt solution and the result is satisfactory except in the case of 42 ml. of bittern. Two grams of oak leaf ash contained 0.232 g. of potassium and 50 ml of urine contained about 0.05 g. of potassium and 0.2 g. of sodium. One hundred milliliters of the bittern contained 4.99 g. of potassium chloride, 5.24 g. of sodium chloride, 24.8 g. of magnesium chloride and 8.36 g. of magnesium sulfate and the results of the experiment indicate that milligram quantities of cesium could successfully be precipitated from considerably dense solutions.

TABLE II

EFFECT OF SEVERAL IONS ON THE RECOVERY OF CESIUM

Total vol. of soln., 100 ml.; conc. HNO_3, 4 ml.; H_3PO_4 (as P), 2 mg.; ^{137}Cs, carrier-free; NH_4 molybdate soln., 10 ml.

Ions	Concn. (%)	^{137}Cs recovery (%)
NH_4^+ (nitrate)	0	99.2
〃	0.01	98.2
〃	0.1	97.2
〃	1	68.0
〃	5	23.7
K^+ (chloride)	1	99.5
〃	5	87.4
〃	10	79.9
〃	20	53.3
Na^+ (chloride)	1	100
〃	2	98.9
〃	5	99.2
〃	10	98.9

Effect of several ions on the recovery of cesium.—The effect of ammonium, potassium and sodium ions on the recovery of carrier-free cesium was examined (Table II). A bulk quantity of those ions which hastened the separation of the precipitate and ammonium ion might decrease the solubility as a result of the common-ion effect. At concentrations above one per cent of ammonium and five per cent of potassium, the precipitate carried no more the cesium tracer completely. Sodium chloride did not interfere with the perfect precipitation at its almost saturated solution.

TABLE III

PRECIPITATION OF VARIOUS AMOUNTS OF CESIUM BY THE PHOSPHOMOLYBDATE METHOD

Total vol. of soln., 100 ml.; conc. HCl, 4 ml.; H_3PO_4 (as P), 2 mg.; NH_4Cl (as NH_4), 100 mg.; Ammonium molybdate soln., 10 ml.; ^{137}Cs activity added, 1750 c.p.m.

Cs taken mg.	Activity carried c. p. m.	Cs recovery %
carrier-free	1718	98.2
0.01	1726	98.6
0.1	1740	99.4
1	1773	101
10	1782	101
100	239	13.6

TABLE IV

CONTAMINATION OF CESIUM AMMONIUM PHOSPHOMOLYBDATE WITH OTHER FISSION ACTIVITIES

Tracer	Carrier	Activity taken c. p. m.	Activity carried c. p. m.	Contamination %	Remarks
^{89}Sr	carrier-free	3.3×10^5	227	0.068	HNO_3 acid
〃	〃	〃	95	0.029	HCl acid
〃	Sr 70 p.p.m.	4.1×10^4	23	0.056	HCl acid
^{144}Ce	carrier-free	$5\ \times10^4$	80	0.16	HNO_3 acid
〃	〃	〃	86	0.17	HCl acid
^{91}Y	〃	$5\ \times10^4$	175	0.35	HNO_3 acid
〃	〃	〃	203	0.40	HCl acid

Effect of the amount of carrier cesium.—For the purpose of determining cesium-137 concentrations in natural materials, a definite quantity of carrier cesium is added prior to the separation procedures, and the measured activity must be corrected for the chemical yield of cesium. To determine a preferable amount of the carrier, and to ditermine whether various amounts of cesium could successfully be precipitated with ammonium phosphomolybdate or not, an experiment was carried out. The result is shown in Table III. From tracer concentrations up to 100 p.p.m. of cesium in acid solution could be perfectly precipitated with ammonium phosphomolybdate in the presence of 20 p.p.m. of phosphorus.

Contamination of cesium ammonium phosphomolybdate with other fission activities.—Contamination of cesium ammonium phosphomolybdate with other radioactive nuclides is a matter of concern when a direct precipitation is performed without scavenging pretreatment. Attention has therefore been centered on isotopes of fairly long half-lives, strontium and cerium. Cesium was precipitated from the solution containing each of the following, strontium-89, cerium-144 and yttrium-91, and the precipitate was mounted for counting. The conditions of the precipitation were the same as described in Table I. The result shown in Table IV indicates good decontamination of each of the nuclides in question.

Contamination with potassium and rubidium.—An accurate estimation of cesium-137 by beta counting will be unsuccessful when the precipitate of cesium ammonium phosphomolybdate is contaminated with rubidium and/or potassium. According to the geochemical studies by one of the authors on the rare alkali elements in biological materials[4], the average weight ratio of K : Rb : Cs was about $10^5 : 10^2 : 1$ for natural plants. A preliminary investigation on the cesium-137 concentration indicated that the isotopic ratio of ^{137}Cs : ^{133}Cs in 1957 was $(1\sim10)\times10^{-8}$ for human urine and Japanese food materials. Thus the disintegration ratio of ^{40}K : ^{87}Rb : ^{137}Cs is calculated to be approximately 200 : 5 : (2∼20). When the radioactivity of cesium-137 is to be measured with an average error of 10% and the contamination with potassium and/or rubidium must be kept less than 2∼3% of the cesium activity, a decontamination factor of 10∼100 is necessary for rubidium and $10^3\sim10^4$ is necessary for potassium.

TABLE V

CONTAMINATION OF AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH POTASSIUM AND RUBIDIUM

Total vol. of soln., 100 ml.; conc. HNO_3, 4 ml.; H_3PO_4 (as P), 2 mg.; NH_4 molybdate soln., 10 ml.

Dissolved element mg.		Found in ppt. mg.	Decontamination factor
K	0.1	n. d.	—
〃	1	n. d.	—
〃	10	n. d.	—
〃	10^2	0.1	10^3
〃	10^3	1.1	9×10^2
〃	10^4	7.3	1.4×10^3
Rb	0.01	n. d.	—
〃	0.1	n. d.	—
〃	1	0.5	2
〃	10	4.3	2.3
〃	10^2	13	7.7

Ammonium phosphomolybdate was precipitated from the solutions containing various amounts of potassium and rubidium and analyzed for those elements by a flame photometry. The result shown in Table V suggests that this single separation is insufficient for the necessary decontamination especially for rubidium. Another step of decontamination is desirable. To meet with this demand, the chloroplatinate precipitation method[3] was adopted because of the great difference of solubilities between the alkali elements including ammonium. The potassium chloroplatinate is approximately 90 times, the ammonium salt 60 times, and the rubidium salt 3 times more soluble in water than the cesium chloroplatinate at 20°C[3]. This method was already proposed for the carrier-free separation of cesium by one of the authors.

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[4] N. Yamagata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 299, 610 (1951).

TABLE VI
PHOSPHATE ELIMINATION BY HOT-WATER EXTRACTION
(200 ml. of human urine)

No.	^{137}Cs added c.p.m.	^{137}Cs extracted c.p.m.	^{137}Cs recovery %	P contained mg.	P extracted mg.
1	1920	1816	94.6	816	110
2	1948	1853	95.2	827	112
3	1937	1809	93.5	686	92.5
4	2111	2003	94.8	356	48.0

Preliminary removal of excessive phosphate and other fission activities.—Biological material contains a bulk quantity of phosphate and the phosphomolybdate precipitation can not be applied directly, because an excess of phosphate and a shortage of ammonium molybdate reagent results in insufficient precipitation of cesium as shown in Table I. When sufficient quantity of the reagent for the perfect precipitation of phosphate is added, a bulky precipitate is formed and the later treatment will become impracticable.

Dry-ashed biological material was treated with hydrochloric - nitric acid mixture (1 : 1) and heated to dryness to destroy the remaining organic matter. If organic matter remains, it may interfere with the precipitation of ammonium phosphomolybdate. The completely dried residue was repeatedly extracted with hot water. The recovery of cesium by the hot-water extraction was checked by a tracer experiment and the result was satisfactory (93.5∼95.2%). By this means, a greater part of phosphate remained insoluble as calcium or magnesium phosphate (Table VI).

The extract was treated with ammonium hydroxide and the phosphates of calcium and magnesium were precipitated. These carried down the tracers of cerium-144 and yttrium-91 almost perfectly and a part of strontium-89. The loss of cesium-137 was only a tenth of one per cent (Table VII).

TABLE VII
REMOVAL OF THE FISSION ACTIVITIES BY PHOSPHATE PRECIPITATION
Total vol. of soln., 150 ml.; Salt soln., 50 ml.; H_3PO_4 (as P), 100 mg.; conc. NH_4OH, 2 ml. excess.

Tracer (carrier-free)	Activity taken c. p. m.	Activity carried c. p. m.	Removal %
^{89}Sr	39853	6703	16.8
^{91}Y	47501	47401	99.8
^{137}Cs	21573	37	0.17
^{144}Ce	64947	64712	99.6

Over-all decontamination and recovery of cesium.—The elimination of other elements and radioactive nuclides by the present method of cesium separation is schematically summarized in Table VIII. The over-all decontamination and the recovery of cesium were determined by an experiment with 75 ml. of salt solution (containing 1.5 g. each of calcium, potassium and sodium, 0.75 g. of magnesium and 0.015 g. of iron). The solution was diluted to about 300 ml. with water after the addition of 10∼30 mg. of cesium carrier, 1 mg. of rubidium and a proper quantity of radioactive tracer. Then, it was treated as described in the following paragraph under separation. The precipitate of cesium chloroplatinate was examined for the presence of ammonium, rubidium, and potassium after being weighed and counted.

TABLE VIII
ELIMINATION OF OTHER ELEMENTS AND NUCLIDES BY THE PRESENT METHOD OF CESIUM SEPARATION

	Procedure	Eliminated elements and nuclides
1st	Phosphate pptn.	Ca, Mg, Fe, Al, Heavy metals ^{144}Ce, ^{91}Y
2nd	NH_4 phosphomolybdate pptn.	Ca, Mg, K, Na ^{144}Ce, ^{89}Sr, ^{91}Y
3rd	Chloroplatinate pptn.	NH_4^+, ^{87}Rb, ^{40}K

Only a trace of ammonium was found in the precipitate. The contribution of the activity of potassium-40 is less than 0.2 dpm, while that of rubidium-87 is calculated as approximately 1 dpm without regard to self absorption. As the beta energy of rubidium-87 is considerably lower (0.275 Mev) than that of cesium-137 (0.52 Mev), the greater absorption minimizes the contribution of contaminated rubidium activity to the cesium activity[1].

A device for cesium-133 determination.—The precipitation of a trace of cesium with ammonium phosphomolybdate is so effective that it can be applied to the determination of natural cesium in biological materials without the addition of a carrier.

The precipitate of cesium ammonium phosphomolybdate is dissolved in ammonium hydroxide. The ammoniacal solution is passed through an anion-exchange resin column (OH-form. For example, φ 8 mm.×150 mm., Diaion SA ♯200). The effluent solution is free from phosphate and molybdate and contains ammonium hydroxide and cesium. The solution is evaporated to expel excess of ammonia and to reduce the volume. After neutralization with a drop of

TABLE IX

OVER-ALL DECONTAMINATION AND RECOVERY OF CESIUM

Cs carrier added mg.	Cs recovery %	Activity added c.p.m.	Activity carried c.p.m.	Decontamination factor	K carried μg	Rb carried μg
10	80.5	—	—	—	93	26
30	93.1	—	—	—	77	20
20 (Sr 1 mg.)	84.8	^{89}Sr 6.6×10^5	2.1	3×10^5	88	13
20	92.7	^{91}Y 9.2×10^5	6.1	1.5×10^5	99	21
20	90.4	^{144}Ce 2.2×10^6	10.2	2×10^5	72	18

hydrochloric acid, the cesium can be determined without interference of any other elements by a flame spectrophotometric technique.

Proposed Procedure

The following procedure is proposed for the determination of cesium-137 in biological materials and soil samples. It has been designed for samples containing approximately 10 μμc of cesium-137 or 1/2~1/7 g. of potassium[5]. An aliquot of the sample must be taken aside before the addition of cesium carrier when the natural cesium-133 is being determined.

Sample Preparation.—*Urine.*—Add 50ml. of nitric acid and 2 ml. of cesium carrier to 500 ml. of urine in a beaker and evaporate to approximately 50 ml. Transfer the solution into a porcelein dish and heat to dryness. Moisten the residue with hydrochloric-nitric acid mixture (1:1) and heat to dryness. Repeat the treatment several times to destroy all of the organic matter. Extract the dried residue with five 50 ml. portions of hot-water and filter. Make up the combined filtrate to approximately 300 ml, and proceed as under separation.

Cereals, Vegetables and Dry Milk.—Dry ash about 300~500 g. of cereals (100~200 g. of dried vegetables, 50 g. of dry milk) at 400~450°C. Extract the ash (or carbonized matter) after the addition of 2 ml. of cesium carrier with five 50 ml. portions of hot hydrochloric acid (1:10) and filter. Transfer the combined filtrate into a porcelein dish and evaporate to dryness after the addition of 50 ml. of nitric acid. Extract the dried residue with five 50 ml. portions of hot-water and filter. Make up the combined filtrate to approximately 300 ml, and proceed as under separation.

Soil (N-ammonium acetate extraction).—Add 3 liters of N-ammonium acetate solution (pH 7) to 300 g. of fresh soil in a 5 liter beaker. Stand the mixture for 4~5 days with occasional agitation, and then filter the supernatant. Evaporate the filtrate after the addition of 2 ml. of cesium carrier in a porcelein dish to dryness. Moisten the residue with hydrochloric-nitric acid mixture (1:1) and heat to dryness. Repeat the treatment several times to destroy all of the organic matter. Extract the dried residue with five 50 ml. portions of hot-water and filter. Make up the combined filtrate to approximately 300 ml, and proceed as under separation.

Separation.—Add ammonium hydroxide dropwise to the solution derived from sample preparation until a dense precipitate of phosphates appears and then add 2 ml. excess of ammonium hydroxide. Allow to settle and test the supernatant liquid for complete precipitation by the addition of ammonium hydroxide. Filter and wash the precipitate with ammonium hydroxide (1:100). Combine the wash solution and the filtrate. Discard the precipitate. Add 20 ml. of nitric acid and 5 mg. of P (as phosphoric acid). Heat the mixture to 50~60°C, then add 20 ml. of 10% ammonium molybdate solution. Agitate vigorously and rub the wall of the beaker with a glass rod to hasten the precipitation. Allow to settle and after cooling filter and wash with 5 portions of nitric acid (2:100). Take up the yellow precipitate with ammonium hydroxide (1:1) and wash thoroughly with water. Boil the combined filtrate and washings until the odour of ammonia disappears. Dilute to 100 ml. with distilled water and cool with cold water. Add 1 ml. of 10% chloroplatinic acid with stirring. Rub the wall of the beaker with a glass rod until yellow precipitate appears. Stand for several hours. Filter through a weighed one inch filter paper mounted on a Hirsch funnel. Wash with 10 ml. of cold water and 3 portions of ethyl alcohol. Dry the filter paper and precipitate at 110°C and

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[5] During 1956~57, milk, rice and human urine in different countries showed a general ^{137}Cs concentration of 20~70 μμc ^{137}Cs/g potassium. (U. N. Scientific Committee on the Effects of Atomic Radiation. A/AC.82/R. 65/Add.3 p. 31, 8 May 1958).

weigh to determine the cesium recovery. Mount the precipitate in a measuring dish for counting. Standardize the counter with a known amount of cesium-137 and 20 mg. of cesium carrier precipitated as the chloroplatinate.

Summary

A simple and rapid separation method for cesium-137 in biological materials has been presented. It is composed of three steps, phosphate elimination, ammonium phosphomolybdate precipitation and chloroplatinate precipitation. The over-all yield of cesium is over 85% and the decontamination from other fission activities is more than 10^5 for cerium-144 and strontium-89. The contribution of the activities of rubidium-87 and potassium-40 is negligibly small in the determination of cesium-137 in biological materials by beta counting.

Kiriu College of Technology
Gunma University, Kiriu