Capture of Radioactive Cesium onto a Phosphomolybdate Precipitate Layer and its Determination

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The object of this research was to find a simple, rapid and accurate method for the determination of radioactive cesium in solutions which are extremely dilute or contain various substances. In the conventional method[1] for the determination of radioactive cesium, the coprecipitation method using a suitable carrier has been mainly adopted. However, that method is incomplete and unsuitable for such sample solutions as mentioned above.

Therefore, a new method is here presented which is based on filtering a sample solution through a precipitate layer of thallium phosphomolybdate and directly measuring the radioactivity of the precipitate on the layer after washing and drying. In this method, the coexistence of various substances scarcely ever interferes with the determination of radioactive cesium and moreover the cesium, even in 2 liters of a solution, is almost completely recovered.

Experimental

Apparatus and Chemicals. — The Shimadzu D-55 type GM-counter, a specially designed glass-filter and a holder as indicated in Fig. 1 were used for the measurement of the radioactivity. Phosphomolybdic acid was prepared by Brauer's method[2] and a 2% solution in 2% nitric acid was used. The thallium solution which contained 1 mg. thallium per 1 ml. of 2% nitric acid was prepared by dissolving metallic thallium in nitric acid. Sodium cobaltinitrite reagent was prepared by Ishibashi's method[3]. Processed cesium-137, thallium-204 and strontium-90 were obtained and diluted to about 1 μC/ml.

Procedure.—Fifty ml. of thallium solution, 4 ml. of concentrated nitric acid and 126 ml. of water were placed in a 300 ml. beaker. Then, 20 ml. of phosphomolybdic acid was added to it. After being concentrated to about 7 ml., the contents were transferred into a glass-filter as shown in Fig. 1, filtered and washed with 2% nitric acid. The washing was continued until only a small amount of washing solution remained on the precipitate layer. Then, the sample solution which was a 2% nitric acid solution containing radioactive cesium was filtered through the previous glass-filter at the rate of 2 drops every 3 seconds or more. At the end of the filteration, the precipitate layer was washed with 2% nitric acid followed by concentrated acetic acid and dried at 120°C for about an hour. Finally, the activity on the precipitate layer was measured by using a holder as shown in Fig. 1 and GM-counter.

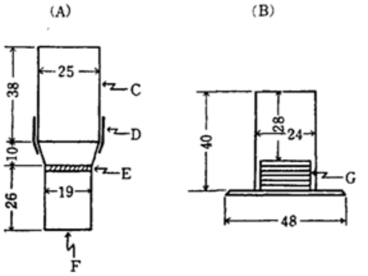

Fig. 1. Glass-filter and holder (unit; mm.)
(A) Glass-filter, separable to C and F
(B) Holder
C; Glass-cylinder
D; Gum
E; Filter-plate
F; Glass-filter, used for the measurement of radioactivity
G; Metallic-plates

Results and Discussion

Reproducibility.—The results obtained

TABLE I
REPRODUCIBILITY OF MEASUREMENTS

No. of sample	Counts per min.
1	3017
2	3032
3	2928
4	2975
5	3071
6	3033
7	2957

Mean value=3002
Max. error=+2.5%

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[1] For example, B. Kahn, D. K. Smith and C. P. Straub, *Anal. Chem.*, **29**, 1210 (1957).

[2] G. Brauer, "Handbuch der Präparativen Anorganishen Chemie", Ferdinand Enke Verlag, Stuttgart (1954), p. 1278.

[3] M. Ishibashi, "Qualitative Analysis", Shōkabō, Tōkyo (1947), p. 25.

with regard to seven samples are shown in Table I. The values for each sample correlate within an error of ±2.5%. Therefore it is believed that the present method can be used adequately for the quantitative determination of radioactive cesium.

Proportionality. — Portions of 0.2, 0.5, 0.8, 1.1, 1.4, 1.7, 2.0 and 2.5 ml. of each radioactive cesium solution were diluted to a 100 ml. of 2% nitric acid solution with nitric acid and water. The results obtained with these samples are indicated in Fig. 2. It is clear that a linear relationship holds between the amount of radioactive cesium in a sample solution and the strength of the activity on the precipitate layer, and the maximum error involved is 8.3% when this calibration curve is used.

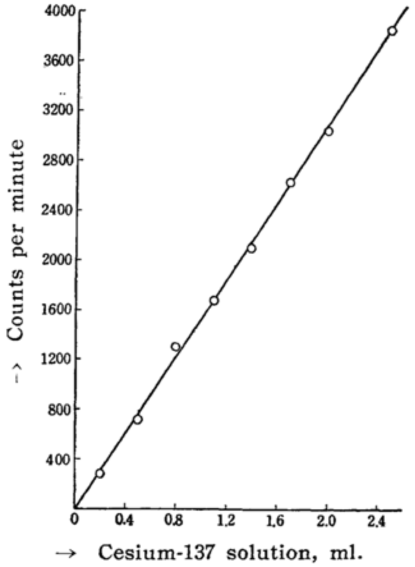

Fig. 2. Calibration curve

Volume of Sample Solution.—Portions of 25, 50, 100, 400, 600, 1000 and 2000 ml. of each sample solution were used in a 2% nitric acid solution which contained about 1 μC of cesium. The results in Table II indicate that the recovery of radioactive cesium is almost complete. Therefore, all the sample solutions in the following experiments will be diluted to 100 ml.

TABLE II

VOLUME OF SAMPLE SOLUTIONS

Volume (ml.)	Counts per min.
25	2974
50	3051
100	2962
400	2985
600	2958
1000	2974
2000	2992

Amount of the Precipitate.—Table III shows the relationship between the amount of the precipitate and the activity of the precipitate for the case where a definite amount of radioactive cesium is used. It is seen from the table that the activity gradually increases in accordance with an increasing amount of the precipitate. Therefore, the amount of the precipitate had better be as definite as possible for accurate measurements.

TABLE III

AMOUNTS OF THE PRECIPITATE

Tl soln. (ml.)	Wt. of ppt. (mg.)	Counts per min.
2	13.6	2548
5	25.8	2669
10	39.5	2712
20	69.1	2762
30	90.5	2849
50	156.7	2986
75	204.3	3113
100	275.0	3123

Concentration of Nitric Acid. — The relationship between the concentration of nitric acid in the sample solution and the activity of the precipitate is shown in Table 4. The data indicate that the activity slowly increases with an increase in the concentration of the nitric acid. However for convenience and economy, in view of the small difference all sample solution were prepared as 2% nitric acid solution.

TABLE IV

CONCENTRATION OF NITRIC ACID IN SAMPLE SOLUTIONS

Concn. of HNO_3 (%)	Counts per min.
0.0	2917
0.5	2957
1.0	2945
2.0	2967
4.0	3013
8.0	3068
16.0	3113

Rate of Filtration. — The relationship between the rate of filtration and the activity of the precipitate is shown in Table V. The results indicate that radioactive cesium is completely captured on the precipitate, when 100 ml. of sample solution is passed as uniformly as possible through the precipitate layer for more than 27 minutes.

TABLE V

VELOCITY OF FILTRATION

Time (min.)	Counts per min.
8	2812
18	2937
27	2997
60	3013
120	3058

Capturing Capacity of Cesium on the Precipitate.—This experiment was made to determine what amount of cesium is captured on a definite amount of the precipitate. The results obtained are shown in Table VI and indicate that an amount of cesium chloride less than 500 μg. is almost completely captured on about 156 mg. of thallium phosphomolybdate.

TABLE VI

CAPTURING CAPACITY OF CESIUM ON THE PRECIPITATE

CsCl taken g.	Activity (cpm)		Wt. of ppt. mg.
	Ppt.	Filt.	
5	3017	0	—
10	2997	0	—
25	3091	0	—
50	3021	0	—
100	3059	0	—
200	2978	0	—
500	3085	0	—
1000	2856	0	157.3
2000	2514	11	157.5
5000	1710	368	156.3
10000	1068	1228	155.4

The radioactive cesium in the filtrate was determined by the cobaltinitrite method using potassium as a carrier. The results obtained in the preliminary experiment are shown in Table VII.

TABLE VII

PRELIMINARY EXPERIMENT BY COBALTINITRITE METHOD

Cesium-137 soln.	K_2SO_4 taken	Counts per min.
0.5 ml.	20 mg.	608
1.0 〃	〃	1206
2.0 〃	〃	2393

Distribution of Cesium on the Precipitate Layer. — This experiment was made to determine how the radioactive cesium was distributed on the precipitate layer. Three different procedures were tested with the same amount of radioactive cesium and the results obtained are shown in Table VIII.

TABLE VIII

DISTRIBUTION OF CESIUM ON THE PRECIPITATE LAYER

Exp. No.	Counts per min.
1	2381
2	3061
3	2405

Exp. 1; Cesium-137 was coprecipitated with thallium phosphomolybdate.
Exp. 2; The present method.
Exp. 3; The precipitate followed by the present method was homogenized.

Judging from the self-absorption by the precipitate and the results indicated in Table VIII, it is inferred that the radioactive cesium dose not uniformly distribute itself in the precipitate layer, but is captured more in the upper layer than in the lower of the precipitate. Moreover, a measurment of the activity by the present method is more sensitive than that by the coprecipitation method. Therefore, the present method is superior to the conventional coprecipitation method.

Solubility of the Precipitate. — This experiment was made to investigate how much precipitate is dissolved when 100 ml. of 2% nitric acid solution is passed through the precipitate layer. The solubility was radiometrically determined by the use of radioactive thallium-204 as a tracer. The results obtained are shown in Table IX and the solubility was found to be 0.18 mg. per 100 ml. of the filtrate at 20.5°C.

TABLE IX

SOLUBILITY OF THE PRECIPITATE

	Ppt. layer	100 ml. of filt.
Wt.	157.6 mg.	?*
cpm	9630	11

* Thallium-204 in the filtrate was precipitated by using the same amount of thallium as that in the precipitate layer.

Mechanism of Cesium Capturing.—These experiments were made to clarify the mechanism by which cesium was captured on the precipitate. 1.47×10^{-4} moles of thallium phosphomolybdate labelled with radioactive thallium-204 was used as the precipitate layer and potassium, rubidium and cesium chloride solution each of which contained 2.94×10^{-4}

moles in 100 ml. of 2% nitric acid, were used as sample solutions, After a sample solution is filtered through the precipitate layer, the radioactive thallium in the filtrate was coprecipitated by adding 25 ml. of 4% potassium iodide solution and 10 ml. of the standard thallium solution to it. Then the radioactivity of the precipitate was measured after filtration, washing and drying. Judging from the results shown in Table X and the other results obtained previously, the radioactive cesium in a sample solution seems to be captured by means of the ion exchange phenomenon. However it is not possible to conclude that all the cesium captured on the precipitate layer depends upon the ion exchange phenomenon.

TABLE X

MECHANISM OF CESIUM CAPTURING

Sample soln.	Radioactivity (cpm)	
	Ppt. layer	filt.
Blank	9454	11
K^+	9457	12
Rb^+	9228	349
Cs^+	8919	590

Influence of Potassium Sulfate. — The relationship between the amount of potassium sulfate and the strength of the activity is shown in Table XI. It is found that less than 1 g. of potassium sulfate in 100 ml. solution does not affect the strength of the activity on the precipitate layer.

TABLE XI

INFLUENCE OF THE POTASSIUM ION

K_2SO_4 (g./100 ml.)	Counts per min.
0.2	3068
0.5	3044
1.0	2974
2.0	2891
4.0	2751
8.0	2518
ca. 12 (Sat. soln.)	1862

Influence of Ammonium Chloride.—The relationship between the amount of ammonium chloride and the intensity of the activity is shown in Table XII. From

TABLE XII

INFLUENCE OF THE AMMONIUM ION

NH_4Cl (g./100 ml.)	Counts per min.
0.1	3008
0.2	2986
0.4	2776
0.8	2448
1.2	2011
2.5	1366
5.0	683

TABLE XIII

INFLUENCE OF THE RUBIDIUM ION

RbCl (mg./100 ml.)	Counts per min.
1	3059
2	3015
4	3016
8	2935
16	2868
32	2561
64	2228

TABLE XIV

Compounds	Wt./100 ml.	Counts per min.
LiCl	2 g.	2984
Na_2SO_4	2 〃	3017
〃	5 〃	2857
$Mg(NO_3)_2$	5 〃	3014
$CaCl_2$	5 〃	3008
$Sr(NO_3)_2$	5 〃	3013
$Ba(NO_3)_2$	5 〃	3008
$Al(NO_3)_3$	5 〃	2889
$Cu(NO_3)_2$	1 〃	2996
$AgNO_3$	1 〃	3017
$Zn(NO_3)_2$	1 〃	3045
$Cd(NO_3)_2$	1 〃	2970
$Hg(NO_3)_2$	1 〃	2999
H_3BO_3	1 〃	3020
$Pb(NO_3)_2$	1 〃	2951
$Fe(NO_3)_3$	1 〃	2912
$Co(NO_3)_2$	1 〃	3081
$Ni(NO_3)_2$	1 〃	2968
NaH_2PO_4	1 〃	3030
$Bi(NO_3)_3$	1 〃	2976
$SnCl_4$	1 〃	3052
$Cr(NO_3)_3$	1 〃	2847
Na_2WO_4	1 〃	1361
$Mn(NO_3)_2$	1 〃	2930
$Th(NO_3)_4$	0.5 〃	3008
$P_2O_5 \cdot 18MoO_3 \cdot aq$	0.5 〃	2985
NaCl	1 〃	3092
KBr	1 〃	3088
KI	1 〃	3075
K_2CrO_4	1 〃	3015
Na_2SO_3	1 〃	2962
$KClO_3$	1 〃	2920
$NaNO_2$	1 〃	1677
$H_2C_2O_4$	1 〃	3058
conc. HCl	5 ml.	2992
conc. H_2SO_4	5 〃	2942
conc. H_3PO_4	5 〃	2969
conc. CH_3COOH	5 〃	2880
$BeSO_4$	50 mg.	2982
$TlNO_3$	2.6 〃	2939
〃	13.0 〃	1113
〃	32.5 〃	373

the table, it is seen that less than 0.2 g. of ammonium chloride in a 100 ml. solution does not affect the activity on the precipitate.

Influence of Rubidium Chloride.—The results obtained in the presence of rubidium chloride are shown in Table XIII. They indicate that less than 8 mg. of rubidium chloride in 100 ml. solution does not affect the activity on the precipitate.

Influence of Other Substances.—The results obtained in the presence of various other substances are shown in Table XIV. For the most part, the substances do not interfere with the determination of radioactive cesium, but the following substances do; thallium, sodium tungstate and sodium nitrite.

Recovery in the Presence of Other Radioactive Elements.—The rare earth nuclides used in this experiment were prepared from a fission products by Yamatera's method[4] in which the fission products were easily divided into ruthenium, cesium, strontium and the rare earth group by use of mineral acids and the ion exchange resin, Dowex-50 (×8). According to the above mentioned method, about 3% of the radioactive strontium and 11% of the radioactive rare earth nuclides were captured on the precipitate layer. However, their interference with the determination of cesium was prevented by the following pretreatment. To the sample solution which contains radioactive cesium and other nuclides were added 5 mg. of ferric iron, 10 mg. of calcium ion and 50 ml. of 1% sodium carbonate solution. After filtration the filtrate was diluted to produce 100 ml. of 2% nitric acid solution. This solution was treated by the same procedure as before.

The results obtained are shown in Table XV. As can be seen from the table, the radioactive cesium is quantitatively recovered by this method in the presence of strontium-90 and rare earth nuclides which are commonly encountered in an aged fission product.

TABLE XV
INFLUENCE OF OTHER RADIOACTIVE NUCLIDES

Sample	Counts per min.
Blank	3014
R. E. N.+Cs	2989
Sr+Cs	2919
R. E. N.+Cs+Sr	2941
F. P.	472
F. P.+Cs	3464

R. E. N.; Rare Earth Nuclides
F. P.; Fission Products

Recovery of Radioactive Cesium from Natural Waters.—This experiment was made to investigate what percentage of cesium was recovered in the case of using one liter of natural water as a sample solution. One liter each of river and sea water were acidified to produce 2% nitric acid solution and filtered through a filter-paper, Tōyō-Roshi No. 5A, after a definite amount of the radioactive cesium was added to it. The same procedure as mentioned above was followed. The results obtained are shown in Table XVI and indicate that about 93% of the radioactive cesium was recovered from one liter of either river or sea water by this method.

TABLE XVI
RECOVERY OF CESIUM-137 FROM NATURAL WATERS

Sample	Counts per min.	Recovery (%)
Blank	3069	100
River water	2842	92.6
Sea water	2864	93.3

Other Results.—In these experiments, the same glass-filters were repeatedly used, but no adverse effects resulted when they were twice boiled with 2N-aqueous ammonia and dilute nitric acid for about an hour.

Summary

(1) Up to 500 μg. cesium dissolved in less than 2 liters of solution is quantitatively captured on the precipitate layer by filtering the cesium solution through it.

(2) The activity on the precipitate is proportional to the amount of cesium-137 present in the solution and consequently, the quantity of cesium-137 is easily determined.

(3) The mechanism of capturing cesium on the precipitate layer is believed to be due to the ion exchange phenomenon.

(4) Determination of the radioactive cesium by this method is not interfered with by the presence of a large amount of various substances except rubidium, cesium, thallium, tungstate and nitrite. Radioactive strontium and rare earth elements also interfere, but their interference may be prevented by pretreatment.

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[4] H. Yamatera, A paper read before the 10th Annual Congress, Chem. Soc. of Japan, April, 1957.

(5) Recovery of the radioactive cesium dissolved in one liter of either river or sea water are about 93%.

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