Carrier-free Separation of Cesium from Fission Products by the Use of Coprecipitation with Thallium(I) Dipicrylaminate

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(Received January 12, 1957)

The authors showed in the previous report[1] an efficient coprecipitation of a trace amount of cesium with thallium (I) dipicrylaminate and suggested several possible ways of its separation from the carrier. The present report deals with its separation from both the carrier ion and other fission activities, including ^{90}Sr–^{90}Y, ^{106}Ru–^{106}Rh, ^{95}Zr–^{95}Nb and rare earth elements.

Coprecipitation of Other Fission Activities with Thallium(I) Dipicrylaminate

The radionuclides which coprecipitate with thallium(I) dipicrylaminate were clarified in order to find the later process of separation.

The radionuclides in question were separated from mixed fission products, about one year old, by ion-exchange method[2] and each fraction was converted into nitric acid solution. Their suitable quantities were submitted to direct precipitation with thallium(I) dipicrylaminate after neutralization with sodium hydroxide.

The following percentages of applied activities were found in the directly precipitated thallium(I) dipicrylaminate.

Rare earth elements	0.20
^{95}Zr–^{95}Nb	0.73
^{90}Sr–^{90}Y	0.53
^{106}Ru–^{106}Rh	0.38
U	56.8[3]

Those figures indicate that some scavenging pretreament is necessary in the practical separation of cesium from mixed fission products.

Separation of Cesium Activity from Thallium(I) Dipicrylaminate

For the separation of cesium activity from thallium(I) carrier, three processes were tested: (1) precipitation, (2) ion-exchange and (3) extraction.

(1) Precipitation. Hydrous ferric oxide carries down various kinds of fission activity, but a negligible amount of cesium. Since the thallium(III) ion was expected to behave similarly, the coprecipitation of fission activities with thallium(III) hydroxide was tested.

An acid solution containing 0.1 m mol. of the thallium(I) ion was mixed with a proper quantity of fission products, oxidized with chlorine water, and neutralized to about pH 9. Immediate filtration

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[1] N. Yamagata, T. Yamagata and S. Watanabe, This Bulletin, **30**, 577 (1957).

[2] K. Kimura et al., *Japan Analyst*, **3**, 335 (1954).

[3] The value for uranium is so high that, when it is present in fission products, it must be previously removed by solvent extraction.

resulted in about 83.6–85.8 % coprecipitation of overall activities. The loss of a trace amount of cesium under the same condition was only 0.3–0.4 % and about 2 % of thallium entered the filtrate; the latter could be removed, however, by extraction or ion-exchange method as described later.

In practice, the starting material is thallium(I) dipicrylaminate containing a trace amount of cesium; the precipitate is dissolved in hot water and acidified with hydrochloric acid. The precipitate of free dipicrylamine can be easily removed by filtration without loss in cesium activity.

(2) Ion-exchange. Since, the selectivity coefficients of Dowex 50 given by W. C. Bauman and J. Eichhorn[4] are 2.04 for K_H^{Cs} and 8.60 for $K_H^{Tl(I)}$, chromatographic separation of cesium from thallium(I) is expected to be easily accomplished, when both elements are present in appreciable amounts. The present investigation, however, concerns the separation of a trace amount of cesium from a large quantity of thallium.

The selectivity coefficients of the cation exchanger Dowex 50 X–12 for cesium and thallium(I) were determined by the batch method described by one of the authors[5]. The results, shown in Table I, indicate that the K_H^{Cs} value for an infinitely dilute solution is greater by twice or more, as compared with the ordinary value. The difficulty, which the simple chromatographic separation involves, was also confirmed by dynamic flow tests.

TABLE I

SELECTIVITY COEFFICIENTS OF THALLIUM(I) AND CESIUM

(Dowex 50, X–12)

Selectivity coefficients		Molar fraction in solution α	Molar fraction in resin β
$K_H^{Tl(I)}$	18.5	0.0119	0.182
	19.8	0.0084	0.143
K_H^{Cs}	5.8	0.078	0.33
	10	0.0060	0.058
	12	5.8×10^{-4}	0.0069
	13	1.1×10^{-8}	1.4×10^{-7}

Another promising method of separation by the use of ion-exchange resin is the utilization of the strong adsorbability of thallium(III) ions upon an anion-exchange resin in hydrochloric acid solution[6]. Selectivity coefficients were determined for three kinds of anion-exchanger by the batch method. Dowex 1 was proved to be the best as shown in Table II, the ion-exchange capacity being 2.72 meq. per gram of resin dried at 72°C. Dynamic flow experiments, by use of ^{204}Tl as an indicator for breakthrough, also proved this method to be satisfactory

TABLE II

SELECTIVITY COEFFICIENTS OF THALLIUM(III) IN HYDROCHLORIC ACID SOLUTION

Concentration of HCl	Anion exchanger	Selectivity coefficient	Molar fraction in solution α	Molar fraction in solution β
1 N	Dowex 1 X–8	370	5.5×10^{-4}	0.170
	Dowex 2 X–10	250	8.1×10^{-4}	0.169
	Amberlite IRA–410	110	1.4×10^{-3}	0.134
4 N	Dowex 1 X–8	3400	9.8×10^{-5}	0.249
	Dowex 2 X–10	820	3.6×10^{-4}	0.226
	Amberlite IRA–410	360	5.9×10^{-4}	0.174

3) Extraction. It is well known that the thallium(III) ion can be extracted from hydrochloric or hydrobromic acid medium with diethyl ether[7]. The authors also determined the efficiency of extraction for the removal of thallium from a trace amount of cesium.

Twenty ml. of the acid solution was shaken with the same volume of diethyl ether, saturated with hydrochloric or hydrobromic acid of corresponding concentration. In the case of 12 N hydrochloric acid and 6 N hydrobromic acid, the procedure was modified so that the acid solution, previously saturated with ether, was shaken with pure ether. When thallium(III) was shaken, several drops of saturated chlorine water were added to avoid possible reduction of thallium.

The results are shown in Table III. The extraction of thallium(III) and the recovery of the cesium activity were satisfactory, when the concentration of acid was kept 1 to 4 N. The results also

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[4] W. C. Bauman and J. Eichhorn, *J. Am. Chem. Soc.*, **69**, 2830 (1947).

[5] N. Yamagata, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **87**, 513 (1957).

[6] K. A. Kraus and F. Nelson, A/Conf. 8/P/837 (1955).

[7] I. Wada and R. Ishii, *Bull. Inst. Phys. Chem. Research, Tokyo* **13**, 264 (1934).

TABLE III
EXTRACTION OF THALLIUM(III) AND OTHER ELEMENTS FROM HYDROCHLORIC AND HYDROBROMIC ACID SOLUTION WITH DIETHYL ETHER

Percentage of the element remaining in HCl solution after one extraction

		Concn. of HCl				
		1 N	2 N	4 N	6 N	12 N
Carrier-free	Tl(III)	0.79	1.6	0.83	2.8	85
0.1 m mol.	Tl(III)	0.69	1.6	0.64	3.2	83
Carrier-free	Cs	98.6	99.8	98.2	99.4	99.2
Mixed F.P.		99.0	—	99.0	99.0	99.0
Tracer	U(VI)	89.3	—	91.2	—	—

Percentage of the element remaining in HBr solution after one extraction

		Concn. of HBr			
		1 N	2 N	4 N	6 N
Carrier-free	Tl(III)	2.5	0.59	1.3	77
0.1 m mol.	Tl(III)	0.41	0.45	1.7	30

indicated that, when 0.1 m mol. of thallium (III) was extracted with ether only once, about 1% or 0.2 mg. of this element entered the cesium solution.

In the practical separation of cesium, the starting material is thallium(I) dipicrylaminate which is insoluble in diethyl ether. An organic solvent, which is immiscible with water and dissolves the precipitate, would be more useful than diethyl ether, because it also removes the free dipicrylamine.

For this purpose, methylisobutyl ketone was found to be the best. It readily dissolves both thallium(I) dipicrylaminate and free dipicrylamine. The extraction of thallium(III) with methylisobutyl ketone was studied from hydrochloric acid solution, and the results are shown in Table IV.

TABLE IV
EXTRACTION OF THALLIUM(III) AND OTHER ELEMENTS FROM HYDROCHLORIC ACID SOLUTION WITH METHYLISOBUTYL KETONE

Persentage of the element remaining in HCl solution after one extraction

	Concn. of HCl			
	1 N	2 N	4 N	6 N
0.1 m mol. Tl(III)	0.89	0.56	1.0	0.73
Carrier-free Cs	99.5	99.6	99.7	99.7
Tracer U(VI)	84.4	—	89.2	—

Proposed Procedure

Step 1. To the sample of fission material[8], add iron(III) and strontium nitrate solution equivalent to 20 mg. of iron and 5 mg. of strontium. Add sodium hydroxide solution of proper strength until the solution is basic to thymol blue (pH 8–9) and then 1 ml. of 1 M sodium carbonate solution. Filter and wash with a little water.

Step 2. After the neutralisation of the filtrate, if necessary, to pH 8–9, add about 100 % excess of sodium dipicrylaminate solution (3 % in water)[9] and cool the resulting solution for about half an hour in ice water. With constant stirring, add 1 ml. of 0.1 N thallium(I) nitrate solution dropwise, and continue the stirring for thirty minutes at 0°C. Filter the precipitate and wash first with 2 ml. of ice water, and then with two 2 ml. portions of diethyl ether at 0°C.

Step 3. Take up the precipitate in 5–10 ml. of methylisobutyl ketone into a separatory funnel. Add 1 ml. of saturated chlorine water and 5–10 ml. of 2 N hydrochloric acid. Shake vigorously for one minute and take the aqueous layer in another separatory funnel.

Step 4. To the separatory funnel, add the same volume of methylisobutyl ketone and shake for one minute vigorously. Evaporate the aqueous layer to dryness in a small counting dish and mount.

The results of recovery and separation tests are shown in Table V. The gross decontamination factor is greater than

TABLE V
RECOVERY AND SEPARATION TESTS

Activities taken cpm		^{137}Cs activity found cpm	Recovered Cs %
F.P.	1.1×10^5	1142	—
F.P.	1.1×10^5		
^{137}Cs	1149	2148	93.8
R.E.	1.5×10^5		
Sr-Y	1×10^4		
Ru-Rh	2×10^4	1002	87.2
Zr-Nb	2×10^3		
^{137}Cs	1149		

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8) The sample must not contain potassium or rubidium, since they will be present in the final product as inert solids and removed with difficulty. If uranium is present in the starting sample, it must be removed previously.

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals" Interscience Pub. Inc., New York (1950), p. 501.

10^4, although the proposed procedure is only valid for about one year old fission products; when cesium is to be prepared from or analyzed in a fresher sample, the procedure should be modified.

Summary

A procedure has been presented for the separation of carrier-free cesium from the fission products. The method makes use of coprecipitation with thallium(I) dipicrylaminate followed by solvent extraction with methylisobutyl ketone in the presence of hydrochloric acid and an oxidizing agent. The recovery of active cesium is about 90% and the gross decontamination factor is more than 10^4.

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