Coprecipitation of a Trace Amount of Cesium with Thallous Salts

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Introduction

Direct separation of carrier-free radioactive cesium-137 from other fission activities has usually been accomplished, in the first step, by the use of the ammonium or the potassium ion as carrier[1]. The second step, the separation of cecium from the carrier ions is, however, fairly difficult, especially from potassium.

Coprecipitation of a trace amount of cesium with a thallous salt can be employed for this purpose, followed by oxidation to thallic state and precipitation as hydroxide.

The following experiments deal with the coprecipitation of a trace amount of cesium with thallous (1) dipicrylaminate, (2) cobaltinitrite, (3) chloroplatinate, (4) phosphotungstate, (5) silicotungstate, (6) phosphomolybdate, (7) copper ferrocyanide, (8) chloride, (9) bromide, (10) iodide and (11) sulfide.

The other well known precipitation methods, such as iodobismuthate, perchlorate and periodate method, were not tested, because these reagents oxidize thallous ions to thallic.

Experimental

The conditions of precipitation and filteration were chosen, from the viewpoint of practical convenience, to facilitate rapid precipitation and immediate filtration.

Unless otherwise specified in the following, the precipitating agent is added to the carrier-free cesium solution (^{137}Cs imported from U. S. A. in 1954, Batch No. 14) and then the thallous nitrate solution with constant agitation. The precipitate is filtered off or centrifuged after thirty minutes' agitation and another thirty minutes' digestion without stirring.

The activity was measured by the use of a Geiger-Muller tube of the mica end-window type and a Tracerlab's "1000"-scaler.

1. Dipicrylaminate Method[2]. — A proper quantity of carrier-free cesium solution (about 10^4 cpm. in 0.3 N hydrochloric acid) is taken in a 50 cc. Erlenmeyer flask and neutralized to thymol blue with 0.1 N sodium hydroxide solution. About 100% excess of 3% magnesium dipicrylaminate solution is added and the mixture is made up to 30 cc. After cooling for about half an hour in ice water, 1 cc. of 0.1 N thallous nitrate solution (containing about 20 mg. thallium) is dripped with constant stirring. The product is stirred for thirty minutes and set aside for another thirty minutes in ice water. The precipitate is filtered off and washed first with 2 cc. of ice water, then with two 2 cc. portions of diethyl ether at 0°C.

The filtrate and the washings are united, made up to 50 cc. with water and 5 cc. portions are evaporated up in small dishes, for their activity (A) to be measured. To the same volume of the solution, one tenth quantity of the radioactive cesium first taken is added and the activity (A′) is measured after evaporation. The activity of cesium removed by coprecipitation (%) is represented as $100(A'-2A)/(A'-A)$.

2. Cobaltinitrite Method[3].—To the carrier-free cesium solution in a flask, the reagent (about 8 cc.), prepared from cobaltous nitrate and sodium nitrite, is added and diluted to 30 cc. Thallous nitrate solution is added dropwise with stirring, at room temperature. The precipitate is filtered off and washed twice with 10% acetic acid solution.

3. Chloroplatinate Method[4].—To the carrier-free cesium solution in a flask, about 50% excess of 5% aqueous chloroplatinic acid solution is added and diluted to 30 cc. The thallous nitrate solution is added dropwise with mechanical stirring, at room temperature. The precipitate is filtered off with a glass filter and washed twice with 98% ethyl alcohol. The solubility of thallous chloroplatinate in water is very small and an anhydrous condition as in the case of potassium determination is not necessary. The precipitate is usually colloidal and filtered with difficulty. With vigorous stirring, however, it becomes crystalline and is easily filtered.

4. Phosphotungstate Method.—To the carrier-free cesium solution in a flask, 2 cc. of 0.1 M solution of the reagent is added and diluted to 30 cc. with 3 N or 6 N hydrochloric acid. At 0°C or 60°C, with stirring, the thallous nitrate solution is added dropwise. The resulting precipitate

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[1] T. Shiokawa and M. Yagi, *Japan Analyst*, **5**, 220 (1956.)

[2] R. B. Hahn and R. O. Backer, AECU-2903 (1955); E. B. Sandell, "Colorimetric Determination of Traces of Metals" London, (1950) p. 501.

[3] R. Overstreet and L. Jacobson, Paper 286 of "Radiochemical Studies: The Fission Products." editted by H. B. Evans, Book 3, New York (1951); F. P. Treadwell and W. T. Hall, "Analytical Chemistry" Vol. 2, 8th ed. John Wiley and Sons, Inc., London (1931) p. 68.

[4] "Gmelins Handbuch der Anorganischen Chemie" System Nr. 38, Verlag Chemie, Berlin (1940) p. 164.

is of colloidal nature and must be separated by centrifuging.

5. Silicotungstate Method[5].—The procedure is similar to that for the phosphotungstate method; 0.1 M solution of silicotungstic acid was used.

6. Phosphomolybdate Method[5].—To the carrier-free cesium solution in a flask are added 18 cc. of 0.15 N nitric acid, 0.15 g. of ammonium molybdate, and 0.3 cc. of conc. phosphoric acid, to be diluted to 30 cc. The thallous nitrate solution is added dropwise with stirring at 40–50°C, for the precipitate to be collected by centrifuging.

7. Copper Ferrocyanide Method[6].—To the carrier-free cesium solution in a flask are added 18 cc. of 0.15 N nitric acid, 5 cc. of 1/15M potassium ferrocyanide solution and the thallous nitrate solution. The resulting solution is cooled to 0°C. Five cc. of 1/20 M copper sulfate solution is added with constant stirring, at 0°C. The precipitate is collected by centrifuge. This method, originally described by H. L. Krieger et at.[6] did not use a thallium carrier.

8. Thallous Chloride Method.—To the carrier-free cesium solution, 3 N hydrochloric acid and distilled water are added to produce 30 cc. of 1 N acid solution. After being cooled to 0°C with constant stirring, this solution is treated with the thallous nitrate solution. The precipitate is filtered off and washed with 1 N hydrochloric acid at 0°C.

9. Thallous Bromide Method.—The cesium solution is submitted to a procedure similar to that mentioned above, by the use of hydrobromic acid.

10. Thallous Iodide Method[7].—Free iodine, occasionally found in hydroiodic acid, may oxidize thallous ion to thallic, interfering with the formation of thallous iodide. Potassium iodide was used instead of hydroiodic acid. To the carrier-free cesium solution in a flask, 1 cc. of glacial acetic acid and 5 cc. of 10% potassium iodide solution are added and diluted to 30 cc. The thallous nitrate solution is added with stirring, at 0°C or at room temperature. The precipitate is filtered off and washed first with 1% solution of potassium iodide in 1% acetic acid and then with acetone.

11. Thallous Sulfide Method.—The carrier-free cesium solution is evaporated up in a flask to eliminate the free hydrochloric acid and treated with the thallous nitrate solution and 5 cc. of 1 N acetic acid. The product is mixed well and neutralized with concentrated ammonia water with further addition of 1 cc. excess. The resulting solution is made up to 30 cc. and, after being heated to 60°C, bubbled with hydrogen sulfide for thirty minutes or for four hours. The precipitate is immediately filtered off and washed with ammoniacal ammonium sulfide solution.

Results and Discussion

The group of methods shown in Table I represents successful coprecipitation; tracer amounts of cesium can be collected almost perfectly by these methods. From the view-point of avoiding contamination with cesium and rubidium which can be introduced from the used reagents containing alkali elements, the cobaltinitrite and the copper ferrocyanide method are not satisfactory. Chloroplatinic acid is rather expensive and is not suitable for practical use. Thus, dipicrylaminate or the phosphotungstate method is recommended, the former being considered to be more suitable. Dipicrylamine is very easily purified from metallic contaminants before use and the thallous salt of dipicrylamine containing cesium activity can be decomposed with a dilute mineral acid to precipitate free dipicrylamine, which is removed by extraction with an organic solvent. The extracted dipicrylamine can be recovered for further use.

The following cautions are, of course, needed for the practical use of this reagent:

1) As the precipitation of thallous dipircylaminate takes place in a slightly alkaline condition, iron, aluminum and other heavy metals must be previously removed.

2) Potassium, ammonium and rubidium ions form a precipitate with dipicrylamine; they must be absent in the solution.

In Table II, the results of unsuccessful coprecipitation are shown. Silicotungstic acid is an effective reagent for coprecipitation of a trace amount of cesium or francium[8], when the cesium ion is used as carrier, but, when the thallous ion is used, it failed to act as a trace-catcher.

Phosphomolybdic acid, which was recommended by H. L. Krieger et al.[6] as an efficient precipitant for cesium, also failed to be so when the thallous ion was used. In those cases, the failure of coprecipitation was supposed to be derived from the difference in crystal structure between cesium and thallous silicotungstate (or phosphomolybdate).

The examination of the separation of cesium activity from thallium and other fission activities is beyond the scope of this article. If any presumption could be possible, however, the results of the methods described in Table II should provide an important suggestion concerning the procedure for separation of thallium

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[5] L. E. Glendenin and C. M. Nelson, Paper 283 of "Radiochemical Studies: The Fission Products" ed. by H. B. Evans, Book 3, New York (1951); E. K. Hyde, *J. Am. Chem. Soc.*, **74**, 4181 (1952).

[6] H. L. Krieger, B. Kahn and C. P. Straub, ORNL-1966 (1955).

[7] "Gmelins Handbuch der Anorganischen Chemie" Syst. Nr. 38, Verlag Chemie, Berlin (1940) p. 160.

[8] E. K. Hyde, *J. Am. Chem. Soc.*, **74**, 4181 (1952).

TABLE I

COPRECIPITATION OF A TRACE AMOUNT OF CESIUM WITH THALLOUS SALTS (1)

Carrier Tl(I) mg.	Activity of carrier-free Cs, added cpm	Activity of Cs, co-precipitated cpm	Activity of Cs, collected %	Chemical yield of precipitation %	Temp. °C	Remarks
(1) Dipicrylaminate method						
20.0	1620	1480	91.4	92.0	0	
20.0	1544	1379	89.3	91.0	0	
40.0	1645	1269	77.1	72.3	18	
40.0	1571	1174	74.7	71.8	18	
(2) Cobaltinitrite method						
20.0	826	768	93.0	—	19	
40.0	1158	1126	97.2	—	19	
(3) Chloroplatinate method						
20.0	1530	1387	90.7	98.9	19	
20.0	1615	1449	95.7	—	19	
(4) Phosphotungstate method						
20.0	1926	1889	98.1	—	60	3 N
20.0	2041	1983	97.2	—	60	6 N
40.0	1950	1940	99.5	—	0	3 N
40.0	2210	2161	97.8	—	0	6 N
(7) Copper ferrocyanide method						
0	2891	2870	99.3	—	0	
20.0	1449	1433	98.9	—	0	
40.0	1498	1484	99.1	—	0	

TABLE II

COPRECIPITATION OF A TRACE AMOUNT OF CESIUM WITH THALLOUS SALTS (2)

Carrier Tl(I) mg.	Activity of carrier-free Cs, added cpm	Activity of Cs, co-precipitated cpm	Activity of Cs, collected %	Chemical yield of precipitation %	Temp. °C	Remarks
(5) Silicotungstate method						
*13.3	1620	1388	85.7	—	0	*Cs-carrier
*13.3	1716	1466	85.4	—	0	
20.0	1655	31	1.9	—	0	3 N
20.0	1603	23	1.4	—	0	6 N
(6) Phosphomolybdate method						
20.0	1422	181	12.7	—	40-50	
40.0	959	57	5.9	—	40-50	
(8) Chloride method						
40.0	1700	160	9.4	89.9	0	
60.0	1491	23	1.6	—	0	
(9) Bromide method						
20.0	1457	34	2.4	96.5	0	
40.0	1658	229	14.1	98.0	0	
(10) Iodide method						
20.0	1898	337	12.5	99.0	18	
20.0	1745	144	8.4	98.5	0	
(11) Sulfide method						
20.0	1610	250	15.5	—	60	30 min.
20.0	1748	33	1.9	—	60	4 hr.

from a trace amount of cesium. Without being oxidized to the thallic state, the thallous ion can be separated from cesium by precipitation as halide or sulfide with a slight loss in cesium activity. The authors also tested the separation of thallium as thallic hydroxide after oxidation with bromine water. The result also proved promising.

Summary

The possibility of coprecipitation of a trace amount of cesium with various thallous salts has been studied. The following salts were proved to be efficient: dipicrylaminate, cobaltinitrite, chloroplatinate, phosphotungstate and copper ferrocyanide; of those the dipicrylaminate method was recommended.

Only partial coprecipitation of cesium took place with thallous silicotungstate, phosphomolybdate, chloride, bromide, iodide and sulfide.

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