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ATOMIC ENERGY OF CANADA LIMITED

Chalk River Project

PHOSPHOTUNGSTATE PRECIPITATION METHOD OF ANALYSIS
OF RADIOACTIVE CESIUM IN SOLUTIONS OF LONG LIVED
FISSION PRODUCT ACTIVITIES

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by

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ABSTRACT

A very rapid and simple procedure is presented for the determination of cesium activity in an aqueous solution of the long lived fission product activities. The procedure consists of the precipitation of Cs as the phosphotungstate from a 5N HNO_3 solution by the addition of phosphotungstic acid. The precipitate is washed twice with 5N HNO_3 , dried and counted. Since the Cs recovery is complete, no radiochemical yield determination is necessary. Self-absorption and self-scattering effects in counting are made to cancel each other by choosing the right amount of Cs carrier. Good decontamination from the other long lived fission product activities and high radiochemical purity are obtained. The method gives a maximum deviation from the average result of less than $\pm 4\%$.

INTRODUCTION

The present laboratory procedure for the determination of radioactive cesium (1) consists of fuming the sample plus 20 mg. of inactive cesium carrier with perchloric acid, followed by precipitation of the cesium perchlorate in absolute alcohol. Any contaminating activities, such as Zr and Nb, are removed by dissolving the precipitate in water and carrying out an Fe(OH)_3 scavenging. The supernatant solution is then evaporated to dryness and heated strongly to completely decompose the ammonium ion introduced in the Fe(OH)_3 scavenging step. The Cs is finally reprecipitated as the perchlorate, filtered, dried, weighed and counted.

As this procedure is time consuming and somewhat hazardous, attempts have been made to develop a shorter method of analysis which eliminated the use of perchloric acid.

EXPERIMENTALi) Reagents

Carrier Solution - Cs carrier - 10 mg. Cs/ml. made up by dissolving 12.7 g. CsCl in 1 liter H_2O

Ru carrier - 10 mg. Ru/ml. made up by dissolving 20.5 g. RuCl_3 in 1 liter H_2O

Zr carrier - 10 mg. Zr/ml. made up by dissolving 29.4 g. $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 1 liter HNO_3

EXPERIMENTAL (Cont'd)i) Reagents (Cont'd)5N HNO₃ solution

0.05M phosphotungstate acid solution - made up by dissolving 66.2 g. phosphotungstate acid anhydride P₂O₅.24W₀₃.25H₂O in 400 ml. H₂O

ii) Procedure

1. The sample aliquot is pipetted into a 12 ml. centrifuge tube containing 6 drops (300 λ) Cs carrier, 1 drop Ru carrier, and 0.5 ml. Zr carrier solutions.
2. The solution is diluted to 8 - 10 ml. with 5N HNO₃ and 1 ml. of 0.05M phosphotungstate acid is added with stirring to precipitate the cesium phosphotungstate.
(Note 1):
3. The mixture is allowed to stand 5 - 10 min., centrifuged, and the supernatant solution is poured off completely.
4. The precipitate is washed thoroughly with 8 - 10 ml. 5N HNO₃, centrifuged, and the supernatant solution is discarded.
5. Step 4 is repeated.
6. The washed precipitate is slurried with 3 - 4 drops H₂O and transferred completely by means of a spitzer onto an aluminum disc. The centrifuge tube and spitzer are then rinsed with small portions of water and the rinsings placed on the disc.
7. The precipitate is dried under an infra-red lamp.

8. The dried precipitate is heated further on a Full-
Control heater for about 30 seconds (Note 2).
9. The precipitate is then counted in a G.M. end window
counter. (Note 3).

NOTES:

1. Before removing the stirring rod from the centrifuge
tube it is always washed free of any precipitate by a
fine stream of water.
2. The precipitate is heated at full heat until an orange-
yellow coloration appears. This usually takes about
30 seconds.
3. No radiochemical yield, self-absorption and self-
scattering corrections are required. The Cs recovery
is complete and the amount of inactive Cs carrier is
so chosen that the self-scattering and self-absorption
effects cancel each other.

iii) Cesium Phophotungstate Precipitation Studies

Radioactive Cs¹³⁷ (10^5 cpm.) and 5 mg. of inactive
Cs carrier (0.5 ml. Cs carrier solution) were precipitated
as the phosphotungstate from 6 ml. of HNO₃ solutions of varying
concentration by the addition of 2 ml. 0.05M phosphotungstic
acid solution. The Cs activity counts found in the supernatant
are shown below.

Normality of HNO ₃	1	2	4	6
% Cs in supernatant	0.02	0.01	N.D.	N.D.

The precipitates were washed twice with 10 ml. portions
of 5N HNO₃ solution. No measurable amounts of Cs activity were

detected in these wash solutions.

This indicates that the cesium phosphotungstate precipitation from 4 - 6N HNO₃ solution is quantitative and that no appreciable amount of Cs is lost in two 5N HNO₃ washes.

iv) Tests on Cs Product Solution

Aliquots from a Cs product solution were carried through the Cs determination procedure using varying amounts of Cs carrier, but no Ru and Zr carriers. At first 6N HCl was used as the precipitating medium and wash solution with the final precipitate dried on a watch glass. This was then replaced by 5N HNO₃ to permit evaporation of the precipitate on an aluminium disc. In the latter determinations, Ru and Zr carriers were used as hold back carriers.

The true Cs activity count for the Cs product solution was obtained by merely pipetting a 50 μ aliquot of the solution onto an aluminium disc and allowing it to dry under an infra-red lamp. The disc was then counted on the top shelf of a G.M. end window counter.

Table I shows the activity counts obtained from the phosphotungstate precipitates after drying under the infra-red lamp, and also after further heating on the Ful-Control. The total Cs activity count, the amount of Cs carrier, the acid medium and the holdback carriers employed are listed in the table.

Table II shows the results obtained from the Cs product solution employing the present laboratory procedure. The final cesium perchlorate precipitate was weighed, and the activity counts corrected for radiochemical yield, self-absorption and self-scattering.

Table I
Analysis of Cesium Product Solution by the
Phosphotungstate Procedure

Sample	Total Count (cpm/ml)	Cs carrier soln. used	Holdback carrier soln. used	Acid used	Count after drying under Infra-red lamp (cpm/ml)	Count after heating on Ful-Control heater (cpm/ml)
1	1.10×10^5	500 λ	none	6N HCl	1.18×10^5	-
2	"	"	"	"	1.19×10^5	-
3	"	"	"	"	1.18×10^5	-
4	"	"	"	"	1.22×10^5	-
5	1.22×10^5	500 λ	none	5N HNO ₃	1.18×10^5	-
6	"	"	"	"	1.15×10^5	-
7	1.22×10^5	500 λ	none	"	1.18×10^5	-
8	"	"	"	"	1.19×10^5	-
9	"	1 ml.	"	"	9.55×10^4	-
10	"	"	"	"	1.12×10^5	-
11	1.19×10^5	"	"	"	1.23×10^5	1.25×10^5
12	"	200 λ	"	"	1.20×10^5	1.26×10^5
13	"	"	"	"	1.21×10^5	1.25×10^5
14	"	"	"	"	1.18×10^5	1.22×10^5
15	1.19×10^5	100 λ	none	5N HNO ₃	1.27×10^5	1.28×10^5
16	"	"	"	"	1.27×10^5	1.32×10^5
17	"	"	"	"	1.28×10^5	1.31×10^5
18	"	"	"	"	1.27×10^5	1.27×10^5
19	1.16×10^5	300 λ	500 λ Zr 1 drop Ru	"	1.13×10^5	1.14×10^5
20	"	"	"	"	1.15×10^5	1.17×10^5
21	"	"	"	"	1.13×10^5	1.16×10^5
22	"	"	"	"	1.17×10^5	1.16×10^5
23	"	"	"	"	-	1.20×10^5
24	"	"	"	"	-	1.16×10^5
25	"	"	"	"	-	1.17×10^5
26	"	"	"	"	-	1.15×10^5

Table II

Analysis of Cesium Product Solution by Lab. Procedure

Sample	Total Count (cpm/cm.)	Activity Count (Corrected for yield, self-scattering and self- absorption) (cpm/ml.)
1	1.16×10^5	1.22×10^5
2		1.20
3		1.21
4		1.24
5		1.20

Analysis of the Cs product solution by the phosphotungstate precipitation method using varying amounts of Cs carrier solution (Table I) gave results which decreased with increasing amounts of Cs carrier, due to the increase in self-absorption within the precipitate. Heating the precipitate on the Ful-Control reduced the self absorption giving higher results. The most satisfactory results were obtained in the Cs carrier region of 0.3 ml. - 0.5 ml. where the self-absorption and self-scattering effects are balancing each other.

The results obtained by the laboratory method (Table II) were consistent, but slightly higher than the total Cs activity count. This may be due to an error in the standardization of the Cs carrier solution for the radiochemical yield determination, or variations in the self-scattering and self-absorption within the precipitate.

v) Decontamination Tests

Tests were completed to study the decontamination obtained from the other long-lived fission product activities by the cesium

phosphotungstate precipitation. Inactive cesium phosphotungstate was precipitated in the presence of each of these activities. The amount carried by the precipitate, expressed as a percentage of the initial activity, is shown in Table III. Also listed is the amount of Cs carrier and holdback carriers used. All precipitates except two were washed twice with 5N HNO_3 , dried and counted in the usual manner. The latter part of the table contains the decontamination obtained by the regular phosphotungstate procedure described in this report.

The cesium phosphotungstate precipitation gave very good decontamination from Ce and Sr-Y activities; better than 99.9% decontamination was obtained. The Zr-Nb and Ru decontamination was only fair (98-99%), but improved considerably with the use of holdback carriers and smaller amounts of Cs carrier. The use of 0.5-1 ml. Zr carrier and 0.2 ml. Cs carrier lowered the Zr-Nb contamination from 1-2% to about 0.1%. The Ru contamination of the phosphotungstate also dropped to close to 0.1% when 0.2 ml. of Cs carrier and 1 drop of Ru carrier was employed. Two HNO_3 washes were found necessary to keep the Ru contamination down.

The aluminium absorption curves (Figure 1) obtained by the phosphotungstate precipitation of Cs in the presence of the other long-lived fission product activities (Curves "C" and "D" are identical to the curve obtained from a Cs product (Curve P).

vi) Comparison of the Phosphotungstate Procedure with the Present Laboratory Method

Four laboratory samples of mixed fission product activities were analyzed by the phosphotungstate precipitation procedure and

Table III

(a) Decontamination Tests on Phosphotungstate Precipitation of Cesium

Activity in Sample	Initial Activity Count (cpm/ml.)	Amount of Cs carrier used (ml.)	Holdback Carrier Used	Activity Count on Phosphotungstate Ppt. (cpm/ml.)	Percent of Initial Count
Sr-Y	4.7×10^5	0.5	-	40	0.01
		0.5	-	30	0.03
		0.5	-	850	0.6
		0.5	-	1.5×10^3	1.1
		0.5	-	690	0.5
		0.5	2 drops Ru	6.5×10^2	0.5
		0.5	1 drop Ru	4.5×10^2	0.3
		0.2	2 drops Ru	4.0×10^2	0.3
		0.2	1 drop Ru	2.1×10^2	0.15
		0.5	-	5.6×10^3	1.8
		0.5	-	3.8×10^3	1.2
		0.5	1 ml. Zr	3.8×10^2	0.12
		0.5	1 ml. Nb	5.9×10^2	0.19
		0.2	1 ml. Zr	3.2×10^2	0.10
		0.2	1 ml. Nb	3.2×10^2	0.10
Zr-Nb	3.2×10^5	0.5	-	40	0.01
		0.5	-	30	0.03
		0.5	-	850	0.6
		0.5	2 drops Ru	1.5×10^3	1.1
		0.5	1 drop Ru	6.5×10^2	0.5
		0.2	2 drops Ru	4.5×10^2	0.3
		0.2	1 drop Ru	2.1×10^2	0.15
		0.5	-	5.6×10^3	1.8
		0.5	-	3.8×10^3	1.2
		0.5	1 ml. Zr	3.8×10^2	0.12
		0.5	1 ml. Nb	5.9×10^2	0.19
		0.2	1 ml. Zr	3.2×10^2	0.10
		0.2	1 ml. Nb	3.2×10^2	0.10

(b) Decontamination Tests on Phosphotungstate PrecipitationMethod for the Determination of Cesium Activity

Activity in Sample	Initial Activity Count (cpm/ml.)	Activity Count on Phosphotungstate Ppt. (cpm/ml.)	Percent of initial count	Remarks
Sr-Y	4.7×10^5	70	0.01	
		60	0.06	
		1.1×10^3	0.78	
		2.0×10^2	0.14	
		3.8×10^2	0.12	
		4.5×10^2	0.14	
Zr-Nb	3.2×10^5			One HNO_3 wash
				Two HNO_3 washes
				One HNO_3 wash
				Two HNO_3 washes

Table IV

Comparison of Radiochemical Cesium Analysis of Mixed Fission
Product Solution by the Phosphotungstate and the Present
Laboratory Procedures

Samples Analyzed	Approximate Activity Cont.					Total Count	Dilution used
	Sr-Y	Ce	Cs	Ru	Zr-Nb		
A	15	60	10	10	3-5	2.2×10^8	5×10^3
B	50	Nil	30	20	3-5	2.9×10^5	2×10^3
C	30	Nil	60	10	3-5	6.7×10^6	50
D	Nil	20	10	10	60	3.9×10^6	10 ²

Sample	Cs Activity Count by Phosphotungstate Procedure (cpm/ml.)	Deviation from average result (%)	Cs Activity Count by Lab. Procedure (cpm/ml.)	Deviation from average result (%)
A	2.19×10^7	-0.4	2.20×10^7	-0.9
	2.14×10^7	-2.8	2.28	+2.5
	2.23×10^7	+1.4	2.09	-5.9
	2.25×10^7	+2.3	2.32	+4.5
	Avg. 2.20×10^7		Avg 2.22×10^7	
B	8.56×10^5	-0.9	8.70×10^5	+0.8
	8.86×10^5	+2.5	8.32×10^5	-3.6
	8.74×10^5	+1.2	8.88×10^5	+2.9
	8.46×10^5	-2.1		
	Avg. 8.64×10^5		Avg 8.63×10^5	
C	4.04×10^5	+2.0	4.03×10^5	-2.2
	4.01×10^5	+1.3	4.04×10^5	-1.9
	3.98×10^5	+0.5	4.28×10^5	+3.8
	3.81×10^5	-3.8		
	Avg. 3.96×10^5		Avg 4.12×10^5	
D	4.46×10^5	-0.2	4.65×10^5	+4.1
	4.40×10^5	-1.5	4.38×10^5	-2.1
	4.64×10^5	+3.7	4.42×10^5	-1.2
	4.40×10^5	-1.5	4.52×10^5	+1.2
	Avg. 4.47×10^5		Avg 4.40×10^5	

by the present laboratory procedure for the determination of radioactive cesium. The samples analyzed and their approximate fission product activity content are listed at the top of Table IV. The table also includes the results obtained by each method and the deviations from the average result for each sample.

The Cs results obtained from the mixed fission product solutions by the phosphotungstate procedure compared favourably with those obtained by the laboratory procedure. The large difference in the average results for sample "C" is due to the unusually high value of 4.28×10^5 in one of the laboratory results and the unusually low phosphotungstate method is as good as that of the laboratory method, giving a maximum deviation from the average result of less than $\pm 4\%$.

vii) Radiochemical Purity Test

The radiochemical purity of the cesium phosphotungstate precipitate was checked by drawing up aluminium absorption curves for the beta radiations from the precipitates obtained from samples "C" and "D" in Table IV. These curves appear in Figure 1. An absorption curve of a cesium phosphotungstate precipitate from a Cs product solution is also included for comparison.

DISCUSSION AND CONCLUSIONS

The phosphotungstate precipitation method described in this report is satisfactory for the determination of radioactive Cs in an aqueous solution of the long-lived fission product activities,

Sr^{90} , Y^{90} , Ce^{144} , Cs^{137} , Ru^{106} , Zr^{95} , and Nb^{95} . The results obtained by the procedure were consistent (maximum deviation of less than $\pm 4\%$) and comparable with those obtained by the present laboratory method.

Decontamination from the other long-lived fission product activities is satisfactory. Less than 0.1% of the initial Ce and Sr-Y activity was carried by the phosphotungstate precipitate. The use of holdback carriers for Ru and Zr-Nb activities reduced their carry through to below 0.2%.

The phosphotungstate procedure is much shorter and less hazardous than the present laboratory procedure. The Cs recovery is quantitative, requiring no radiochemical yield determination. The amount of Cs carrier has been so chosen that the self-absorption and self-scattering effects in the final precipitate cancel each other, eliminating self-absorption and self-scattering corrections. The method also eliminates the use of perchloric acid which is a dangerous and explosive reagent.

The radiochemical purity of the phosphotungstate precipitate is high, based on aluminium absorption curves.

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FIGURE I.

