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DETERMINATION OF RADIOACTIVE CESIUM
IN FISSION PRODUCTS

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2903

DETERMINATION OF RADIOACTIVE CESIUM IN FISSION PRODUCTS

Methods commonly used for the determination of radioactive cesium in fission products involve the precipitation of cesium bismuth iodide (3) or the precipitation of cesium perchlorate (5). These methods are not entirely satisfactory. The cesium bismuth iodide method requires a double precipitation followed by a final precipitation as cesium chloroplatinate. This procedure is complicated and requires the use of costly chloroplatinic acid. The perchlorate method requires working under anhydrous conditions and involves the use of explosive perchloric acid. Because of these difficulties, this study was made in which other reagents were investigated.

The problem of finding a reagent which will separate cesium from other alkali metals is not encountered in the analysis of fission product mixtures since rubidium, potassium and the other alkali metals are not present to any appreciable extent (4). Therefore, any method used for the gravimetric determination of potassium probably could also be applied to cesium. Among these methods are the following: precipitation as chloroplatinates (12), perchlorates (12), picrates (1), chlorostannates (6), fluosilicates (8), dipicrylamines (11), and periodates (13).

Dipicrylamine and periodic acid were considered most promising, hence they were investigated for use as reagents for the determination of radioactive cesium in fission products.

209 1 2

PRECIPITATION WITH DIPICRYLAMINE

Dipicrylamine (2, 2', 4, 4', 6, 6' hexanitro diphenylamine) was first used by Poluektov (7) for the detection of potassium. Sheintsis (9) later showed that it could be used for the gravimetric determination of potassium, rubidium, and cesium. These elements form difficulty soluble, crystalline salts with the reagent. In these determinations the magnesium salt of depicrylamine is used as the precipitant. Quantitative precipitation is achieved by adding an excess of the reagent to cold, slightly acid aqueous solutions containing potassium, cesium or rubidium ions.

EXPERIMENTAL

Reagents

Potassium Chloride. 19.0665 g. of chemically pure potassium chloride was dissolved in enough distilled water to make one liter of solution. This solution was standardized by precipitation of potassium perchlorate according to the procedure of Glendenin and Nelson (5). This solution was found to contain 9.90 mg of K^+ per ml.

Cesium Chloride. 12.6680 g. of chemically pure cesium chloride (Foote Mineral Co.) was dissolved in enough distilled water to make one liter of solution. This solution was standardized by the same procedure as used for the potassium chloride (5). This solution was found to contain 9.80 mg of Cs^+ per ml.

Dipicrylamine (2, 2', 4, 4', 6, 6' hexamitrodephenylamine, Eastman Kodak Co.). A 3% solution of the magnesium salt was prepared by dissolving 12 g. of dipicrylamine in 500 ml. of water then adding 5 g. of magnesium oxide. The mixture was stirred for an hour, allowed to stand for 24 hours then filtered.

Cesium ¹³⁴. This radioactive isotope was obtained from the Isotopes Division of the Oak Ridge National Laboratory. This was diluted with 1M hydrochloric acid to bring samples in the counting range. Cesium ¹³⁴ has a half life of 2.3 years and is a beta and gamma emitter.

Standards were prepared by evaporating known amounts of the diluted solution on small watch glasses then counting the beta particles using a mica window G-M tube (Tracerlab TGC-1) and scaler (Nuclear Instrument Model 162).

Procedure The procedure used for the determination of radioactive cesium was adopted from the procedure given by Welcher (11). Two series were run; one in which cesium chloride was used as carrier, another in which potassium chloride was used. An outline of the procedure follows:

(1) Add a known amount of standard carrier solution of cesium chloride or potassium chloride (2-10 mg of Cs or K) to a 40 ml. centrifuge tube, then add a known amount of the solution to be analyzed for radioactive cesium.

(2) Add a drop of thymol blue indicator then neutralize using sodium hydroxide or hydrochloric acid as the case may be.

(3) Add 2 ml of 3% magnesium dipicrylamine reagent for each 5 mg of cesium carrier used or

Add 5 ml of 3% magnesium dipicrylamine reagent for each 5 mg of potassium carrier used.

(4) Stir thoroughly then cool the mixture in an ice bath. Let stand for one hour with occasional stirring.

(5) Filter using a 1.5 cm filter paper disc in a Hirsch funnel. Wash with 5 ml of ice water then with 10 ml of diethyl ether.

(6) Dry for one hour at 80° - 90° C, then weigh and count the precipitate.

(7) Correct for gravimetric yield. The factors used are

$$\frac{\text{Cs}}{\text{Cs D.P.A.}} = 0.2327$$

$$\frac{\text{K}}{\text{K D.P.A.}} = 0.08191$$

The above procedure was followed using varying amounts of cesium chloride as carrier, then repeated using varying amounts of potassium chloride as carrier. The results are given in Tables Ia and Ib.

2908

-5-

TABLE Ia

Determination of Cesium with Dipicrylamine
Using Cesium as Carrier

grams cesium taken	grams cesium recovered	gravi- metric yield	count corrected for background	count corrected to 100% yield	Standard Count	Radio- Chemical Yield
0.0049	0.0030	61.9%	732 cpm.	1183 cpm.	1070 cpm.	110%
0.0049	0.0035	71.9	829 "	1153 "	1070 "	107%
0.0049	0.0034	69.9	822 "	1176 "	1070 "	109%
0.0029	0.0027	93.1	1045 "	1122 "	1070 "	104%
0.0029	0.0025	66.2	976 "	1132 "	1070 "	105%
0.0049	0.0045	91.8	977 "	1064 "	1070 "	99.4%
0.0049	0.0042	85.7	921 "	1075 "	1070 "	100.4%
0.0049	0.0044	89.8	1048 "	1167 "	1070 "	109%
0.0049	0.0043	87.8	768 "	875 "	842 "	103%
0.0049	0.0044	89.8	796 "	886 "	842 "	105%
0.0098	0.0089	90.8	784 "	863 "	842 "	102%
0.0098	0.0087	88.8	756 "	851 "	842 "	101%

TABLE Ib

Determination of Cesium with Dipicrylamine
Using Potassium as Carrier

grams potas- sium taken	grams potas- sium recovered	gravi- metric yield	count corrected for background	count corrected to 100% yield	Standard Count	Radio- Chemical Yield
0.0029	0.0019	66 %	590 cpm.	894 cpm.	890 cpm.	100.4%
0.0029	0.0021	72	710 "	985 "	890 "	110
0.0029	0.0018	82	614 "	990 "	890 "	111
0.0049	0.0040	81.5	700 "	990 "	890 "	96.7
0.0049	0.0040	81.5	700 "	860 "	890 "	96.7
0.0049	0.0041	83.5	720 "	860 "	890 "	96.8
0.0049	0.0036	73.5	700 "	862 "	890 "	105
0.0049	0.0038	77.5	668 "	952 "	890 "	97
0.0049	0.0040	81.5	707 "	863 "	890 "	97.6

209 6

2908

-6-

Separation Studies. In order to study the efficiency of separation of cesium from other activities, the previous procedure was carried out but activities other than cesium were added. It was found that a single precipitation with dipicrylamine did not achieve a good separation from the following activities: Zr^{95} , Nb^{95} , Sr^{90} , Ru^{106} , and Ce^{144} . The separation from strontium was especially poor.

In order to improve the separation the use of scavenging agents and holdback carriers was studied. The following method was found to give good results:

Procedure

- (1) Add 1.00 ml of cesium chloride (or potassium chloride) carrier solution (5.0 mg of Cs^+ or K^+) to a 50 ml centrifuge tube.
- (2) Add a known volume of the activities to be analyzed.
- (3) Add 1/2 ml each of ferric chloride and strontium nitrate solutions. (These solutions contain 10 mg of Fe^{+++} and 10 mg of Sr^{++} per ml).
- (4) Add 1M sodium carbonate solution, drop by drop with stirring until the solution is basic then add 1 ml in excess.
- (5) Centrifuge down and discard the precipitate of $Fe(OH)_3$ and $SrCO_3$.
- (6) Add 1/2 ml each of ferric chloride and strontium nitrate solutions. Centrifuge and discard precipitate.
- (7) Repeat step 6.

209

7

-7-

(8) Add a drop of thymol blue indicator then neutralize with dilute hydrochloric acid.

(9) Add 1 ml of strontium nitrate solution as a hold-back carrier.

(10) Add 5 ml of 3% magnesium dipicrylamine reagent.

(11) Stir thoroughly then cool in an ice bath. Let stand for one hour then filter, wash, weigh, and count the precipitate as directed previously.

The efficiency of the above procedure was checked by analyzing various mixtures of fission products. Both potassium chloride and cesium chloride were used as carriers. The results are given in Table II.

These results show that three scavenging steps are required to remove foreign activities. Very little cesium is lost in the scavenging operations. The above method is therefore recommended for the determination of radioactive cesium in fission products.

TABLE II

Separation Studies **

	grams carrier added	grams carrier recovered	gravi- metric yield	count corrected for background	count corrected to 100% yield	Standard Count	Radiochemical Yield
one	0.0049	cesium	0.0043	89.0%	800 cpm.	870 cpm.	
scav-	0.0098	cesium	0.0090	92.0%	1080 cpm.	1170 cpm.	
enging	0.0049	potassium	0.0036	73.5%	420 cpm.	570 cpm.	
step	0.0098	potassium	0.0080	82.0%	2400 cpm.	2900 cpm.	
two	0.0049	cesium	0.0038	77.5%	600 cpm.	775 cpm.	
scav-	0.0049	cesium	0.0039	79.5%	660 cpm.	830 cpm.	
enging	0.0049	potassium	0.0037	75.5%	350 cpm.	464 cpm.	
steps	0.0049	potassium	0.0038	77.5%	422 cpm.	544 cpm.	
three	0.0049	cesium	0.0036	73.5%	28 cpm.	38 cpm.	
scav-	0.0049	cesium	0.0035	71.5%	29 cpm.	40 cpm.	
enging	0.0049	potassium	0.0039	79.5%	19 cpm.	24 cpm.	
steps	0.0049	potassium	0.0038	77.5%	23 cpm.	30 cpm.	
*	0.0049	cesium	0.0038	77.5%	747 cpm.	957 cpm.	925 cpm. 103%
*	0.0049	cesium	0.0037	75.5%	736 cpm.	975 cpm.	925 cpm. 105%
*	0.0049	potassium	0.0037	75.5%	736 cpm.	975 cpm.	925 cpm. 105%
*	0.0049	potassium	0.0036	73.5%	666 cpm.	907 cpm.	925 cpm. 98%

** The following activities were added to all samples: 1.7×10^4 cpm Ce^{144} , 1.2×10^5 cpm Sr^{90} , 1.2×10^4 cpm Ru^{106} , 2.8×10^4 cpm Zr^{95} - Nb^{95} .

* 925 cpm Cs^{134} added.

PRECIPITATION WITH PERIODIC ACID

Periodic acid was recommended as a precipitant for potassium by Willard and Boyle (13). In this method potassium is precipitated as the slightly soluble salt of periodic acid which is dried and weighed.

Experimental

Known amounts of radioactive cesium along with potassium chloride (or cesium chloride) carrier were precipitated with periodic acid using the procedure given by Willard and Boyle. The precipitates were dried, weighed, then counted. The results are given in Tables IIIa and IIIb.

The above results show that very little carrying of cesium takes place on potassium periodate. Even with cesium periodate the results were not quantitative. Because of these poor results, no further investigations were made with periodic acid.

2908

TABLE IIIa

Determination of Cesium with Periodic Acid
Using Cesium as Carrier

grams cesium taken	grams cesium recovered	gravi- metric yield	count corrected for background	count corrected to 100% yield	Standard Count	Radio- Chemical Yield
0.0029	0.0027	93.2%	700 cpm.	751 cpm.	870 "	86.4%
0.0029	0.0028	96.5	721 "	747 "	870 "	85.8
0.0029	0.0026	89.5	426 "	470 "	870 "	55.0
0.0029	0.0026	89.5	431 "	483 "	870 "	55.5
0.0049	0.0047	96.0	783 "	817 "	870 "	93.8
0.0049	0.0046	94.0	717 "	762 "	870 "	87.5
0.0049	0.0045	91.8	440 "	479 "	870 "	55.2
0.0049	0.0046	94.0	750 "	798 "	870 "	91.7

TABLE IIIb

Determination of Cesium with Periodic Acid
Using Potassium as Carrier

grams potas- sium taken	grams potas- sium recovered	gravi- metric yield	count corrected for background	count corrected to 100% yield	Standard Count	Radio- Chemical Yield
0.0029	0.0027	93.2%	54 cpm.	58 "	870 "	6.6 %
0.0029	0.0026	89.5	15 "	16 "	870 "	1.93
0.0029	0.0026	89.5	20 "	21 "	870 "	2.45
0.0029	0.0027	93.2	70 "	75 "	870 "	6.65
0.0049	0.0046	94.0	18 "	16 "	870 "	1.84
0.0049	0.0046	94.0	82 "	66 "	870 "	7.57
0.0049	0.0047	96.0	90 "	93 "	870 "	10.8
0.0049	0.0047	96.0	65 "	67 "	870 "	7.76

209

11

PRECIPITATION AS CESIUM ALUMINUM SULFATE

Cesium forms a slightly soluble "alum" having the formula $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. (2) This substance was investigated as a possible precipitate for the radiochemical determination of cesium.

Experimental

A known amount of cesium chloride carrier was treated with an excess of saturated aluminum sulfate solution. A crystalline precipitate of cesium aluminum sulfate formed immediately. This precipitate was filtered, washed and then dried at various temperatures.

A constant weight could not be obtained by air drying. Precipitates dried at 110°C . reached a constant weight, but the composition was of the precipitate indeterminate because of water of crystallization remaining. Because of these erratic results cesium aluminum sulfate was found unsuitable as a method for the determination of cesium.

20 7/8 12

2908

-12-

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203

13

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