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PRELIMINARY INVESTIGATION  
OF METHODS FOR THE DETERMINATION  
OF PLUTONIUM IN CHALK RIVER  
DISSOLVER SOLUTIONS



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ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director

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Preliminary Investigation of Methods for the Determination  
of Plutonium in Chalk River Dissolver Solutions.

F. L. Moore and W. S. Lyon

Date Issued: NOV 30 1951

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Abstract

A preliminary study of possible methods for the determination of plutonium in Chalk River dissolver solutions has been made. A direct gross alpha method, with corrections for alpha emitters other than plutonium, appears most desirable and may allow the determination of 99% or more of the plutonium. The TTA method appears to offer a desirable alternate method allowing a plutonium determination of  $98.8 \pm 0.6\%$ . The lanthanum fluoride method gives the lowest yields of the three methods allowing a plutonium determination of  $96.9 \pm 1.6\%$ .

From a survey of possible methods for isotopic Pu<sup>239</sup> - Pu<sup>240</sup> analysis it appears that a mass spectrometric method will be most desirable.

Introduction

Oak Ridge National Laboratory will have a problem of assaying Chalk River dissolver solutions for plutonium for the purpose of determining payment to the Canadians. Three possible methods for the determination of total plutonium alpha activity are the lanthanum fluoride method, the TTA method and the direct gross method. In addition to a method for total plutonium, another method must also be available for the accurate determination of Pu(239) - Pu(240) ratios, since the high neutron fluxes now in use at Chalk River will cause a considerable (~10%) production of Pu(240). Five possible methods for the determination of Pu(239) - Pu(240) ratios are suggested: (1) pulse analysis (2) specific activity determination (3) fission counting (4) activation analysis, and (5) mass spectrometer determination.

Each method for the determination of total plutonium and of Pu(239) -

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Pu(240) ratios is considered below.

Experimental Results

A. Methods for Total Plutonium Alpha Activity. Three synthetic solutions, described in Table I, were prepared to simulate as nearly as possible the Chalk River dissolver solutions of 1:100 dilution in 1 M nitric acid.

Table I

Compositions of Simulated Chalk River Dissolver Solutions of 1:100

Dilution

(All Solutions Prepared in 1 M HNO<sub>3</sub>)

<u>Solution</u>	<u>Uranium (mg/ml)</u>	<u>Plutonium (cpm/ml)</u>	<u>Americium (cpm/ml)</u>
A	4.73	--	--
B	4.73	9859	--
C	4.79	9859	899

Solution "A" was used to indicate the uranium following through the methods and solution "B" was used to indicate the uranium + plutonium following through the methods. Solution "C", which contained all the anticipated alpha emitters, was used to indicate the behavior of the various alpha emitters in a mixture. No curium tracer was available for this work but the behavior of curium in these systems is assumed to be identical with that of americium. The standard lanthanum fluoride method<sup>(6)</sup> has been revised slightly.

I. Lanthanum Fluoride Method

A. LaF<sub>3</sub> Procedure for Plutonium, Americium and Curium.

(a) Take a 1 ml aliquot of the 1:100 dilution in a 3 ml

- centrifuge cone. Add 1 drop of lanthanum carrier (5 mg/ml) and mix well. Add 6 drops of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (5 M) and 6 drops of HF (48%). Stir well with platinum stirrer and digest for 5 minutes. Centrifuge for 5 minutes.
- (b) Add 1 drop of lanthanum carrier. Stir supernatant well and digest for 5 minutes. Centrifuge for 5 minutes and remove supernatant through a capillary tube by suction.
- (c) Wash the precipitate twice with 0.5 ml portions of 1 M  $\text{HNO}_3$  - 1 M HF. Centrifuge each time for 5 minutes.
- (d) Slurry the precipitate with 2 drops of 1 M  $\text{HNO}_3$ , transfer to a stainless steel (or platinum) plate, wash the tube with two additional portions of 1 M  $\text{HNO}_3$  transferring the washes to the plate, dry under an infra-red heat lamp, flame to a dull red heat and count the alpha particles (Pu + Am + Cm).

B. LaF<sub>3</sub> Procedure for Americium and Curium

- (a) Take a 1 ml aliquot of the 1:100 dilution in a 3 ml centrifuge cone. Add 1 drop of lanthanum carrier (5 mg/ml) and mix well.
- (b) Add 2 drops of 0.34 M  $\text{K}_2\text{Cr}_2\text{O}_7$ . Heat in a water bath at 90° C for 15 minutes.
- (c) Add 6 drops of HF (48%) and stir well. Allow to digest for 5 minutes and then centrifuge for 5 minutes. Add another drop of lanthanum carrier. Stir the supernatant well and allow to digest for 5 minutes. Remove supernatant.
- (d) Wash the precipitate twice with 0.5 ml portions of 1 M  $\text{HNO}_3$  - 1 M HF. Centrifuge each time for 5 minutes.

(e) Slurry the precipitate with 2 drops of 1 M HNO<sub>3</sub>, transfer to a stainless steel (or platinum) plate, wash the tube with two additional portions of 1 M HNO<sub>3</sub> transferring the washes to the plate, dry under an infra-red heat lamp, flame to a dull red heat and count the alpha particles (Am + Cm).

To show that negligible amounts of uranium follow through the method, 1 ml aliquots of solution "A" were analyzed by the LaF<sub>3</sub> method (Table II). The geometry was 52%. Each value represents an individual analysis.

Table II  
Uranium Following Through the Lanthanum Fluoride Method

Procedure in the LaF <sub>3</sub> Method	Uranium Alpha After Two Washes	Activity Found (Cpm) After Three Washes
Pu + Am + Cm	11, 11, 16 12, 15, 14 14, 15	13, 14 13, 11
Am + Cm	11, 11, 11 11, 12, 12 13, 15, 10 8, 12, 12, 12	12, 11, 10 13, 10, 11 13, 12

In order to show that a negligible amount of plutonium follows through the Am + Cm procedure, solution "B" was analyzed by the Am + Cm procedure. Table III shows that excellent separation is effected and also indicates the recovery of plutonium when the Pu + Am + Cm procedure was used.

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Table III

The Behavior of Plutonium in the Two LaF<sub>3</sub> Procedures

Analysis of Solution B

Procedure	$\alpha$ C/M Carried
Am + Cm	16, 17, 15 18, 13, 20 4, 21
Pu + Am + Cm	9402, 9425, 9652, 9545 9493, 9537, 9384, 9687 9621, 9442, 9483, 9908 9420, 9476, 9495, 9848  Mean = 9551 = 96.9% Std. deviation = 1.6%

Finally, solution C containing all the anticipated alpha activities was analyzed by the two procedures. Table IV shows the recoveries to be expected in each method.

Table IV

Total Alpha Activity Follow Through in the Two LaF<sub>3</sub> Procedures

Analysis of Solution C

<u>Procedure</u>	<u>α C/M Carried</u>	
Pu + Am + Cm	10,459	10,274
	10,484	10,256
	10,306	10,375
	10,260	10,408
	10,252	
	Mean = 10,342 = 96.1%	
	Std. deviation = 0.8%	
Am + Cm	850, 859, 871, 837	
	837, 865, 859, 872	
	842, 866	
	Mean = 856 = 95.2%	
	Std. deviation = 1.5%	

In the above work when 4 mil platinum plates were used in place of the stainless steel plates the increase in recovered alpha counts was negligible. The LaF<sub>3</sub> method in general has been observed in this laboratory to give  $97 \pm 2\%$  of the gross plutonium when very carefully done. The average recovery in Table III is  $96.9 \pm 1.6\%$  while in Table IV the average total recovery is  $96.1 \pm 0.8\%$  and the Am recovery is  $95.2 \pm 1.5\%$ . It is apparent that an empirical correction factor could be used to give accurate results with a precision better than 1% if several replicates are run.

II. TTA Method

The TTA method used at this laboratory offers an alternate method for determining total plutonium. This method will be tested more thoroughly when actual process dissolver solutions are available. The possible presence of polymeric plutonium must not be overlooked and would make the determination by TTA more complicated.

The three synthetic solutions described in Table I above were

carried through the following TTA method.

TTA Procedure

A. Place a 1 ml aliquot of the synthetic solution in a 30 ml separatory funnel or other suitable extraction vessel. Add 1 ml of 1 M HNO<sub>3</sub>.

B. Extract for 10 minutes with 2 ml of a 0.5 M solution of TTA in xylene.

C. Draw off most of the aqueous phase and discard. Centrifuge the organic phase in a 2 ml volumetric flask for three minutes. Remove the aqueous phase from the bottom of the flask with a transfer pipet. Make the organic phase up to 2 ml with xylene. Mix thoroughly and centrifuge again. Place a 200 aliquot on a stainless steel plate which has been edged with a very thin film of silicone stopcock grease. Dry under an infra-red heat lamp, flame to a dull red heat and count the alpha particles.

(Note: Since these synthetic solutions contained Pu(IV) no adjustment of valence states was used. In actual dissolver solutions it will be necessary to use the standard NH<sub>2</sub>OH.HCl - NaNO<sub>2</sub> treatment.)

The results in Table V indicate that negligible amounts of uranium or americium were extracted while the plutonium recovery was very good (98.8 ± 0.6%).

Table V

TTA Extraction of Synthetic Chalk River Dissolver Solutions

<u>Solution*</u>	<u>α C/M Extracted</u>
A	5, 0, 10, 0
B	9840, 9835, 9750, 9780
C	9730, 9880, 9710, 9660, 9740, 9750

\*See Table I for composition.

III. Direct Gross Method

A direct gross method<sup>(5)</sup> for the determination of plutonium in uranium solutions has been developed. The investigators found that a direct gross gives negligible self-absorption as long as less than 0.25  $\lambda$  of 2 M UNH is evaporated on a plate.

Some work has been done in this laboratory using the direct gross technique. It appears that the gross alpha activity may be determined accurately on a small aliquot of the Chalk River dissolver solutions then, by subtracting the uranium alpha activity (uranium determined colorimetrically) and the americium-curium activity (determined by  $\text{LaF}_3$  analysis), the plutonium content is found. The method would also be more rapid than the other methods and would not be subject to the inherent losses of the other methods. Application of this method will be investigated when actual Chalk River type dissolver solutions are available. It is felt that the direct gross method may permit the determination of 99% or more of the plutonium.

In order to check the direct gross method, a synthetic dissolver solution (1:100) was prepared, consisting of 4.5 mg of uranium per milliliter, 34,167 cpm of plutonium per milliliter and 6,183 cpm of americium per milliliter, all in 1 M  $\text{HNO}_3$ . 25  $\lambda$  aliquots were placed on a stainless steel plate. The pipets were washed three times with 1 M nitric acid.

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Table VI

Data for Determination of Plutonium by Gross Alpha Method

Alpha Activity (cpm/ml)				
From Colorimetric Uranium Analysis	From Am-Cm Analysis			
		Gross		
3578	5932	44,480	42,920	43,280
3578	5926	43,840	43,040	43,560
	5920	43,240	43,080	43,240
	5926	44,440	43,960	Ave. 43,560

\*Calculated from measurement of 25  $\lambda$  samples.

From these data the plutonium may be calculated as follows:

$$\text{Total plutonium found, cpm/ml} = 43,560 - (3578 + 5926) = 34,056.$$

B. Methods for Plutonium<sup>239</sup> - Plutonium<sup>240</sup> Mixtures.

1. Pulse Analysis. Fairstein<sup>(3)</sup> of the Instrument Development Group of the Chemistry Division advises that the energy difference between Pu<sup>239</sup> and Pu<sup>240</sup> alpha particles (50 Kev) is too small to make pulse analysis feasible.

2. Specific Activity Determination. While ostensibly the simplest method (i.e. determination of total plutonium then counting and determination of the amount of Pu<sup>240</sup> by the apparent specific activity), this procedure is considerably complicated by the presence of plutonium isotopes other than Pu<sup>239</sup> and Pu<sup>240</sup>. The determination of total plutonium in these solutions might prove difficult, and the handling of considerable amounts of the hot solution would be required. Probably a high degree of chemical purity would be needed, necessitating considerable laboratory operation.

3. Fission Counting

a. Spontaneous Fission Counting of Pu<sup>240</sup>. The method has been attempted recently at Hanford<sup>(2)</sup>. Counting rates are quite low,

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and the amount of total Pu in any one sample is limited by absorption effects. The specific fission decay rate of Pu<sup>240</sup> is  $1.66 \times 10^6$  fission/gm/hr<sup>(7)</sup>. Good agreement at Hanford has been obtained between calculated Pu<sup>240</sup> and that observed by spontaneous fission counting. Alkire and Miller<sup>(1)</sup> report agreement within 1% between calculated and observed values on 293 g/T material. Experiments are under way at Hanford in an effort to improve techniques. The method is useful in that it gives a direct determination of Pu<sup>240</sup> content. Unfortunately, a relatively large amount of solid-free plutonium is required.

b. Neutron Induced Fission Counting. Instrumentation presents difficulties in this method since there is an extremely high alpha background from the plutonium. Assuming that this problem can be solved, and that absorption within the sample itself is negligible, the method would still be questionable because of the uncertainty in the cross-section for fission of Pu<sup>240</sup>. Studier, et al<sup>(8)</sup> found that the fission cross section for Pu<sup>240</sup> may be as high as 123 barns (if the half-life is 6000 years). The fission cross-section for Pu<sup>239</sup> is 765 barns. At present the half-life is known only to about 5%. Until the fission cross-section for Pu<sup>240</sup> is determined accurately, the method must be classified as uncertain.

4. Activation Analysis. Activation analysis suffers the same uncertainties as neutron induced fission counting. In addition the chemical separation procedures are time-consuming and subject to error.

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5. Mass Spectrometric Analysis. Under the direction of R. F. Hibbs, a laboratory is being set up at Y-12 to handle plutonium mass assays. Hibbs<sup>(4)</sup> believes that by using mass spectrometric methods, accuracy within 1% of the Pu<sup>239</sup> content will be possible. Accuracy to 1 - 2% of the total Pu<sup>240</sup> (i.e. 1 - 2% of ~10%) can also be obtained. The method would require about 25 µg of plutonium and the sample could be delivered to Y-12 as the nitrate solution. Several hours would be required for analysis completion. Hibbs anticipates no difficulty in reducing the assays to routine operations. Isotopes of plutonium other than Pu<sup>239</sup> and Pu<sup>240</sup> could be determined if desired. This method seems to be the most simple accurate, and probably the cheapest yet studied.

#### Summary

Preliminary studies of three methods for the determination of total plutonium in Chalk River dissolver solution indicate that the direct gross method is the most practical. Based on the limited work done to date, the TTA method appears to be a good alternate method. The lanthanum fluoride method gives the lowest yields of the three.

A survey of possible methods for the isotopic analysis of Pu<sup>239</sup> - Pu<sup>240</sup> indicates that the mass spectrometric method is the most practical.

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