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THE IMPURITY ANALYSIS OF PLUTONIUM
PEROXIDE AND PLUTONIUM FLUORIDE

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CONTRACT AT(29-1)-1106

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ABSTRACT

A review has been made of the spectrographic methods used for the impurity analysis of plutonium peroxide and plutonium fluoride. For comparison purposes, the impurity analyses on nitrate feeds, peroxides, fluorides, and metal buttons are reported.

SUMMARY

Spectrographic methods were used for the impurity analysis of plutonium peroxide and fluoride. The peroxide and fluoride were converted to oxide which was analyzed for impurities using the routine pyroelectric carrier distillation methods.

The spectrographic results on four types of samples (nitrate feeds, peroxides, fluorides, and metal buttons) are recorded in tabular form to facilitate a direct comparison between the various production steps. The peroxide precipitation step reduces the average impurity level from 1.62 percent in the nitrate feed to 0.24 percent in the peroxide. The impurity level in the fluorides is approximately the same as that found in the peroxides and about twice that found in the metal buttons.

INTRODUCTION

Plutonium is purified from solutions of scrap at Rocky Flats by a process which utilizes (1) precipitation of plutonium peroxide, (2) calcination of the peroxide, (3) hydrofluorination to plutonium tetrafluoride, and (4) reduction to metal with calcium. To provide information on the purification achieved during these chemical conversions, methods were set up for spectrographic impurity analyses of plutonium peroxide and fluoride samples.

The samples analyzed were selected so that the analytical results would be of some significance to the Production Development Group. The impurity analyses for nitrate feeds and metal buttons, which are routinely analyzed, have also been included for comparison purposes.

EXPERIMENTAL

PLUTONIUM PEROXIDE

The condition of the samples received varied from a wet sludge to a dry powder. The samples were dried at 110°C and the loss of weight recorded. The dry residue was subsequently muffled at 800°C for one hour and the weight loss determined. The plutonium concentration was calculated from the weight of PuO_2 formed after adjusting for the impurities present. The plutonium oxide was analyzed for impurities by the pyroelectric carrier distillation methods⁽¹⁾ used routinely for plutonium metal analysis.

PLUTONIUM FLUORIDE

Using a pyrohydrolytic apparatus⁽²⁾, the plutonium tetrafluoride samples were converted to plutonium oxide by superheated steam. The fluoride concentration was determined by titrating the hydrogen fluoride released during the pyrohydrolysis. The plutonium oxide was analyzed for impurities using the same methods employed for the metal analysis.

RESULTS

The spectrographic results are summarized in Tables I and II. An impurity comparison between peroxides and fluorides, prepared from nitrate feed, is given in Table I. A comparison between fluorides and

(1) C. F. Metz, Anal. Chem. 29, 1748 (1957).

(2) E. Vejvoda, "The Pyrohydrolysis of Plutonium Fluoride", USAEC Report RFP-601, to be published. (Unclassified)

TABLE I

PURIFICATION OF PLUTONIUM DURING CONVERSION
OF NITRATE TO PEROXIDE AND FLUORIDE

Sample Description	No.	Al	Au	B	Ba	Ca	Cr	Cu	Fe	Ga	K	Ng	Mn	Mo	Na	Ni	P	Pb	Si	Sn	Sr
Feed	36	72	L50	1450	L10	218	L50	218	4786	5800	L25	725	72	648	-	2175	-	1088	-	432	-
Peroxide	39	10	10	2	50	200	25	15	613	1	50	20	10	L10	50	40	1500	150	20	40	L10
Fluoride	64	5	15	L0.1	40	50	60	L15	113	L1	45	20	L10	L10	15	35	200	200	L12	14	15
Peroxide ¹	38	20	L10	1.5	50	150	L5	L15	206	L1	10	40	L10	L10	200	L3	750	200	12	30	L10
Fluoride	63	3	L10	0.1	50	300	35	15	320	1	120	30	10	L10	30	5000	L100	160	12	5	L10
Peroxide ¹	46	8	20	1	30	300	75	L15	825	20	1.5	15	L10	L10	50	60	500	150	12	2	L10
Fluoride	81	2	10	L0.1	70	140	300	L15	L100	L1	L1	40	L10	20	60	1250	L100	100	L12	2	20
Peroxide ¹	47	10	40	2	30	200	95	L15	1007	L1	1.5	20	10	L10	50	275	650	400	L12	4	L10
Fluoride	82	8	25	L0.1	50	200	500	L15	L100	L1	100	30	L10	20	20	1500	L100	200	L12	2	30
Feed	16	125	L50	1500	L10	250	L50	300	9000	4500	L25	600	125	L10	-	1800	-	4500	-	1500	-
Peroxide	80	10	L10	L0.1	100	50	25	L15	401	L1	1	5	L10	L10	30	30	650	500	12	400	L20
Fluoride	83	8	25	L0.1	170	100	750	L15	764	L1	50	20	10	L10	35	500	L100	400	L12	110	20
Feed	54	50	L50	1000	L10	75	L50	150	1750	4000	100	300	L10	125	-	1250	-	400	-	50	-
Peroxide	107	20	50	0.2	100	100	20	L15	225	L1	20	20	L10	L10	200	10	750	400	16	6	L10
Fluoride	125	5	125	2	160	200	20	L15	179	L1	50	20	L10	L10	20	50	L100	400	35	3	20
Feed	96	500	L50	664	17	332	250	166	830	L5	415	83	34	34	-	120	-	3320	-	1660	-
Peroxide	132	10	25	0.4	50	500	40	L15	316	L1	L1	10	L10	25	50	25	1000	500	30	400	L10
Fluoride	133	2	10	0.2	70	1000	50	L15	560	L1	30	15	15	L10	10	450	L100	400	L12	75	15
Feed	Not analyzed																				
Peroxide	269	8	L10	1.0	100	400	15	L15	290	L1	5	30	L10	25	70	20	800	175	L12	40	L10
Fluoride	287	5	10	0.4	80	200	55	L15	345	L1	L1	40	10	20	15	1000	L100	160	40	2	20

NOTE: All the above values are reported in $\mu\text{g/g}$ of Pu (ppm).

L = Less Than

1 = Feed No. 36

TABLE II
IMPURITY COMPARISON BETWEEN FLUORIDE AND METAL

<u>Sample</u> <u>Description</u>	<u>No.</u>	<u>Al</u>	<u>Au</u>	<u>B</u>	<u>Ba</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Ga</u>	<u>K</u>
Fluoride	-	30	L10	0.5	L10	500	15	10	231	L1	5
Metal	150	20	L10	0.2	L10	20	10	10	213	L1	L1
Fluoride	-	10	25	0.8	50	500	100	40	243	L1	L1
Metal	508	5	25	0.1	L10	40	40	20	335	Δ	L1
Fluoride	-	5	10	0.8	100	500	75	40	143	L1	L1
Metal	971	10	L10	L0.1	L10	L1	10	L15	239	Δ	L1
Fluoride	126	2	35	L0.1	70	✓	250	L15	400	L1	60
Metal	113	15	L10	0.1	L10	1	20	L15	420	Δ	L1
		<u>Mg</u>	<u>Mn</u>	<u>Mo</u>	<u>Na</u>	<u>Ni</u>	<u>P</u>	<u>Pb</u>	<u>Si</u>	<u>Sn</u>	<u>Sr</u>
Fluoride	-	10	L10	L10	30	40	100	80	12	1.2	L10
Metal	150	200	L10	L10	L1	20	100	L5	30	1.2	L10
Fluoride	-	50	L10	L10	L1	50	L100	100	L12	6	L10
Metal	508	500	L10	L10	L1	50	L100	10	20	1.2	L10
Fluoride	-	20	L10	L10	L1	50	L100	150	L12	3	L10
Metal	971	50	L10	L10	L1	50	200	L5	20	0.4	L10
Fluoride	126	15	L10	L10	13	2000	L100	400	4	20	L10
Metal	113	200	L10	L10	L1	400	L100	75	16	25	L10

NOTE: All the above values are reported in $\mu\text{g/g}$ of Pu.

L = Less Than

✓ = Calcium had been added before sampling.

metal buttons prepared solely from each corresponding fluoride is shown in Table II.

A more complete analysis of each sample is made in Table III for the same feed material and in Table IV for different feed material.

TABLE III
ANALYTICAL RESULTS ON THE CONVERSION
INTERMEDIATES FROM THE SAME FEED

<u>Nitrate Feed</u>				
Sample No.	36			
Plutonium	137.9 g/l			
Impurities	1.77%			
<u>Peroxides</u>				
Sample No.	38	39	46	47
Loss at 110°C	62.25%	52.17%	30.20%	28.15%
Loss at 800°C	68.25%	59.64%	42.55%	47.89%
Plutonium	27.72%	35.25%	50.29%	45.62%
Impurities	0.17%	0.29%	0.21%	0.28%
<u>Fluorides</u>				
Sample No.	63	64	81	82
Fluoride	23.59%	17.46%	21.58%	22.53%
Plutonium	75.27%	76.64%	74.86%	75.54%
Impurities	0.61%	0.08%	0.21%	0.27%

Note: Impurities are based on the plutonium concentration of each sample.

TABLE IV

ANALYTICAL RESULTS ON THE CONVERSION
INTERMEDIATES FROM DIFFERENT FEEDS

	<u>Nitrate Feed</u>			
Sample No.	16	54	96	254
Plutonium	166.2 g/l	200.2 g/l	59.9 g/l	156.3 g/l
Impurities	2.49%	0.93%	0.85%	No Spec Anal

	<u>Peroxides</u>			
Sample No.	80	107	132	269
Loss at 110°C	51.99%	47.74%	62.11%	44.64%
Loss at 800°C	60.08%	55.45%	68.61%	54.06%
Plutonium	34.94%	39.05%	27.25%	40.27%
Impurities	0.22%	0.19%	0.30%	0.20%

	<u>Fluorides</u>			
Sample No.	83	125	133	287
Fluoride	22.52%	21.74%	22.48%	23.15%
Plutonium	75.52%	75.91%	75.50%	75.84%
Impurities	0.30%	0.13%	0.27%	0.20%

Note: Impurities are based on the plutonium concentration of each sample.

PEROXIDE ANALYSIS

Two methods were considered for the impurity analysis of plutonium peroxide: (1) the dissolution of the peroxide with nitric acid after which the solution is analyzed as a nitrate feed sample; and (2) the calcination of the peroxide to oxide after which the oxide is analyzed as a metal sample. Both methods were tried. Method (2) was easier to carry out and no problems were encountered as the peroxides were easily converted to plutonium oxide. However, for method (1), the complete dissolution of the sample was not always attainable. Therefore, the results in this report were obtained by method (2).

The spectrographic results in Table I indicate the efficiency of the peroxide precipitation. Although the quantity of data is limited, it is nevertheless interesting to compare the efficiency of the separation for individual elements. Using the simple expression given by (1),

$$\frac{\text{Average ppm Value in Feed}}{\text{Average ppm Value in Peroxide}} = \text{Separation Factor (1)},$$

the following separation factors were calculated: Al - 11, B - 711, Cu - 14, Fe - 86, Ga - 1229, Mg - 31, Mo - 37, Ni - 27, Pb - 6, and Sn - 6. Individual ppm values indicated as "less than" were calculated in the average by using the numerical value after the "less than" sign. The efficiency of the separation varied as shown by the results on individual peroxide strikes for the same feed material. The peroxide No. 47 (Table I) had the poorest separation for boron, iron, lead, and nickel, while peroxide No. 38 had a more successful separation.

Very little separation, if any, is accomplished for calcium which probably precipitates as calcium sulfate upon the addition of sulfate prior to precipitation with hydrogen peroxide. The peroxide also seems to have barium present, although very little was detected in the feeds. However, the barium may also be concentrated by precipitation as barium sulfate or it may be an impurity of the hydrogen peroxide.

For several of the peroxides in Tables III and IV, a rather large variation is evident for the loss at 110°C. Consequently, the amount of plutonium available for fluorination is also limited.

FLUORIDE ANALYSIS

The only method considered for the impurity analysis was the conversion of the fluoride to oxide after which the oxide was analyzed as a metal sample. Generally, the impurities found in the peroxide are also present in the fluoride. However, from Table I it is evident that chromium and nickel are introduced into the fluoride. The average chromium concentration is six times higher in the fluoride, while the nickel concentration is 21 times higher than in the peroxide. Potassium contaminations were also observed for some of the fluoride samples.

A substantial reduction in the phosphorus concentration was observed for the fluorides. Sodium and aluminum concentrations were less in the fluoride than in the peroxide.

The impurity comparison between fluorides and metals presented in Table II indicates the reduction process reduces the concentrations of Ba, Ca, Cr, K, Na, and Pb. However, the magnesium concentration is substantially increased.

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