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THE PYROHYDROLYSIS OF PLUTONIUM TETRAFLUORIDE

by

E. Vejvoda

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

THE DOW CHEMICAL COMPANY
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GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
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ABSTRACT

A procedure has been developed for the determination of fluorine and plutonium in plutonium tetrafluoride based on the pyrohydrolytic decomposition of the plutonium tetrafluoride.

SUMMARY

A pyrohydrolytic apparatus has been used for the determination of fluoride in plutonium tetrafluoride and to convert the fluoride to plutonium oxide which is used for spectrographic impurity analysis.

The components of the pyrohydrolytic furnace which were in contact with the steam and HF were fabricated from nickel while the remaining parts were made from stainless steel.

The plutonium tetrafluoride is weighed into a platinum boat and placed in the reaction tube which is maintained at a temperature of 850°C. The fluoride sample is hydrolyzed in a stream of superheated steam obtained from a steam generator and preheated to 600°C before entering the reaction tube. The hydrogen fluoride produced is trapped in the steam condensate and titrated to a phenolphthalein end point with standard sodium hydroxide.

For many of the samples analyzed, plutonium was found in the condensate. Consequently, before titrating, sodium citrate, which had previously been neutralized, was added to the condensate to keep the plutonium from hydrolyzing.

The standard deviation for 42 determinations on 15 different plutonium tetrafluoride samples was ± 0.20 percent fluorine. A pure UF_4 sample was used for studying the recovery of fluoride. The average recovery value for 22 determinations was 98.8 percent of the calculated value.

INTRODUCTION

The impurity analysis of plutonium tetrafluoride is usually accomplished by converting the plutonium tetrafluoride to plutonium oxide and analyzing the oxide spectrographically using the pyroelectric carrier distillation method. The conversion from tetrafluoride to oxide is carried out by air oxidation at elevated temperatures. However, the conversion often proceeds with difficulty and is not always complete. When traces of tetrafluoride are present in the oxide being analyzed spectrographically, plutonium is swept into the arc from the more volatile plutonium tetrafluoride. Excitation of the plutonium gives a line-rich plutonium spectrum which obscures the impurity spectrum.

The conversion of tetrafluoride to oxide is readily accomplished by employing high-temperature steam; whereby the reaction proceeds according to equation (1):

Consequently, the pyrohydrolysis of the tetrafluoride appeared to be an excellent way to obtain plutonium oxide for the spectrographic analysis. From equation (1) it is apparent that the fluoride and plutonium concentrations can also be determined by titrating the HF released and weighing the PuO_2 formed.

A pyrohydrolytic apparatus, similar to that described by Susano, White, and Lee⁽¹⁾, was fabricated using nickel instead of platinum for the reaction tube.

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EXPERIMENTAL

APPARATUS

The major components of the pyrohydrolytic apparatus are as follows:

1. Reaction tube, nickel, 22 inches in length and 1-inch outer diameter.
2. Preheater tube, nickel, 18 inches in length and 1-inch outer diameter with an attached 4-inch nickel pipe, 1/2-inch outer diameter, which is connected to a source of steam.
3. Delivery tube, nickel, 13 inches in length and 1/2-inch outer diameter.
4. Sample port, 316 stainless steel, ball and socket door type, opening and closing by lever action.
5. Reservoir drain, 316 stainless steel, cylindrical in shape, 5 inches in diameter and 2 inches in height with a drain valve fastened to the bottom of the reservoir.
6. Hevi-Duty, 4-inch split organic combustion furnace is used to preheat the steam. The power supply is controlled by a Variac variable auto transformer.
7. Hevi-Duty, 12-inch split organic combustion furnace is used to heat the reaction tube. The power supply is controlled by a Variac variable auto transformer.
8. Two calibrated pyrometers with chromel-alumel thermocouples are used to measure the temperatures of the furnaces.
9. Condenser, 316 stainless steel, water cooled, cylindrical in shape, 2 inches in diameter and 9 inches in height.
10. Combustion boats, platinum, 3-inches long by 1/2-inch wide by 3/8-inch high.

The component parts of the apparatus are assembled according to Figure 1. A one-liter 3-necked round-bottom flask heated by a hemispherical Glas-Col mantle controlled by a Variac and partially filled with water is used as a source of steam.

The apparatus is supported on a box-like steel frame which has adjustable cross pieces for regulating the elevation of the equipment.

FIGURE 1. PYROHYDROLYTIC APPARATUS

REAGENTS

Reagent-grade chemicals and distilled water were used in the preparation of all the reagents and in the procedure followed.

1. Sodium citrate, 20-percent solution by weight.
2. Standard 0.1400 N sodium hydroxide (carbonate free) which was standardized with potassium hydrogen phthalate in the prescribed manner.
3. Phenolphthalein indicator was prepared in the usual manner.

PROCEDURE FOR FLUORIDE DETERMINATION

The reaction tube is brought to a temperature of $850^{\circ}\text{C} \pm 25^{\circ}$ while the preheater tube is simultaneously raised to a temperature of $600^{\circ}\text{C} \pm 25^{\circ}$. After these temperatures have been obtained, steam is passed through the system for at least 10 minutes. The steam flow rate is regulated so that approximately 4-5 grams of steam condensate are collected per minute. From 300-500 milligrams of the plutonium tetrafluoride sample are weighed into a tared platinum combustion boat. One hundred milliliters of a 20-percent sodium citrate solution, which has been neutralized with NaOH to a phenolphthalein end point, is placed in a 400-ml fluorothene beaker. The beaker serves as the receiving vessel.

The delivery tube is immersed in the citrate solution to a depth of a few millimeters from the bottom of the receiving vessel. The combustion boat with the sample is placed in the center of the reaction tube. Care must be taken to close the sample port door as quickly as possible once the sample is placed in the reaction tube. The pyrohydrolysis is continued for 20 minutes maintaining the selected temperatures and steam rate. The receiving vessel is removed and the delivery tube is thoroughly washed with distilled water. The washings are added to the receiving vessel. The hydrogen fluoride trapped in the receiving vessel is titrated to a phenolphthalein end point using standard sodium hydroxide. Duplicate determinations are made for each sample.

PROCEDURE FOR PLUTONIUM DETERMINATION

Determining the plutonium concentration by weighing the plutonium oxide formed during the pyrohydrolysis was discontinued since plutonium was often found in the steam condensate. Therefore, the plutonium assay was obtained by weighing the plutonium oxide formed by the air conversion of the tetrafluoride to oxide at 1000°C.

Three-hundred milligrams of the sample $\pm$ 50 mg are weighed into a tared 35-ml platinum dish. The sample is arranged in the dish so as to expose a maximum surface area. The dish is placed in a cold muffle (room temperature) and the door is left slightly ajar to provide for air circulation. The temperature of the muffle is raised to 800°C, upon which the door is completely closed and the temperature raised to 1000°C. After muffling the sample for one hour at 1000°C, the sample is removed and permitted to attain room temperature. The dish is weighed and the weight of the PuO_2 is recorded. The impurities present in the PuO_2 are determined spectrographically and a summation of their oxide concentrations is used in calculating the amount of plutonium present in the sample. Duplicate determinations are made for each sample.

IMPURITY ANALYSIS

The plutonium oxide obtained from the pyrohydrolysis is analyzed spectrographically for elemental impurities. The pyroelectric carrier distillation method is employed for the analysis. The procedure followed is described by Metz⁽²⁾.

RESULTS

Two processes have been used to produce plutonium tetrafluoride: (1) a batch process, and (2) a continuous process. Samples from each process have been analyzed for fluoride, plutonium, and impurities. A summary is presented in Table I.

TABLE I
ANALYSIS OF PLUTONIUM TETRAFLUORIDE

<u>Sample No.</u>	<u>Percent</u>		
	<u>Fluoride</u>	<u>Plutonium</u>	<u>Impurities</u>
Continuous Process			
739	22.92	75.78	0.14
764	20.04	74.20	0.20
774	17.85	75.64	0.21
776	20.77	76.66	0.26
779	21.64	76.54	0.14
795	21.93	75.58	0.61
800	23.36	75.05	0.33
Batch Process			
314	22.62	76.20	0.08
321	23.40	75.95	0.09
325	20.72	77.37	0.11
328	22.66	76.04	0.08
555	20.38	73.80	0.14
700-5	23.24	75.28	0.46
700-6	22.53	75.54	0.20
709	23.14	75.84	0.15

PRECISION

Forty-two fluoride determinations were made on 15 samples. The standard deviation was ± 0.20 percent fluorine and the relative standard deviation was 0.92 percent. Forty-four plutonium determinations were

made on the same 15 samples. The standard deviation was ± 0.12 percent and the relative standard deviation was 0.16 percent. A summary of the precision data for the fluoride analyses is given in Table II, while the precision for the plutonium analyses is presented in Table III.

TABLE II
FLUORIDE RESULTS

Continuous Process							
Sample No.	<u>739</u>	<u>764</u>	<u>774</u>	<u>776</u>	<u>779</u>	<u>795</u>	<u>800</u>
Percent Fluoride	22.96	20.45	17.75	20.67	21.92	21.96	23.40
	22.81	19.91	17.74	20.57	21.66	21.82	21.82
	22.99	20.12	18.06	21.12	21.35	22.00	
		19.66		20.73			
Average	22.92	20.04	17.85	20.77	21.64	21.93	23.36

Batch Process								
Sample No.	<u>314</u>	<u>321</u>	<u>325</u>	<u>328</u>	<u>555</u>	<u>700-5</u>	<u>700-6</u>	<u>709</u>
Percent Fluoride	22.54	23.34	20.59	22.60	20.64	23.36	22.61	23.27
	22.71	23.28	20.81	22.72	20.40	23.48	22.45	23.02
		23.57	20.76		20.10			
Average	22.62	23.40	20.72	22.66	20.38	23.24	22.53	23.14

TABLE III
PLUTONIUM RESULTS

Continuous Process								
Sample No.	<u>739</u>	<u>764</u>	<u>774</u>	<u>776</u>	<u>779</u>	<u>795</u>	<u>800</u>	
Percent Plutonium	75.72	74.12	75.65	76.67	76.60	75.50	75.09	
	75.91	74.46	75.45	76.64	76.49	75.66	75.01	
	75.78	73.99	75.87					
	75.70	74.25	75.60					
Average	75.78	74.20	75.64	76.66	76.54	75.58	75.05	
Batch Process								
Sample No.	<u>314</u>	<u>321</u>	<u>325</u>	<u>328</u>	<u>555</u>	<u>700-5</u>	<u>700-6</u>	<u>709</u>
Percent Plutonium	76.12	75.94	77.43	76.05	73.98	75.22	75.52	75.83
	76.46	75.96	77.27	76.01	73.73	75.35	75.56	75.84
	76.18		77.47		73.73			
	76.04		77.32		73.76			
	76.16							
	76.22							
Average	76.20	75.95	77.37	76.04	73.80	75.28	75.54	75.84

ACCURACY

For studying the accuracy of the method, a pure uranium tetrafluoride sample was used since no pure plutonium tetrafluoride was available. The fluoride concentration was determined by assuming all the uranium present was in the form of uranium tetrafluoride. The uranium concentration was determined gravimetrically and by a chemical titration with potassium dichromate. The average uranium value was used to calculate the fluoride concentration. Twenty-two determinations were made over a period of three months by six different analysts. The average recovery was 98.8 percent of the fluoride present, or 0.3 percent lower than the calculated value. The lowest recovery was 96.3 percent, while the highest recovery was 101.0 percent.

IMPURITY ANALYSIS

The elemental impurities in the plutonium fluoride samples were determined spectrographically and are reported in Table IV. The average total impurity level (3563 ppm) appeared to be higher in the continuous process material than in the batch process material (2189 ppm).

TABLE IV
IMPURITY ANALYSIS

	Sample No.														
	739	764	774	776	779	795	800	314	321	325	328	555	700-5	700-6	709
Ag	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	75	<10	<10	<10
Al	5	100	10	20	15	50	200	30	10	5	5	30	3	8	5
As	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Au	10	<10	<10	<10	<10	25	75	<10	25	<10	10	<10	<10	25	10
B	<.1	.2	.2	<.1	.8	.1	<.1	.5	.8	1.5	.8	.1	.1	<.1	.4
Ba	80	40	80	75	30	150	80	<25	50	50	100	35	50	50	80
Be	<.1	<.1	<.1	<.1	.3	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	.1	<.1
Bi	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ca	200	300	200	200	400	500	200	500	500	500	500	250	300	200	200
Cd	<10	100	50	75	100	<10	<10	<10	<10	10	10	<10	<10	<10	<10
Cr	20	15	200	200	<5	500	60	15	100	75	75	75	35	500	55
Cu	<15	30	15	20	<15	40	20	<15	40	30	40	80	15	5	<15
Cs	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
Fe	208	354	610	648	300	1325	1110	231	243	124	143	264	320	<100	345
Ga	<1	200	75	100	<1	20	10	<1	<1	<1	<1	<1	1	<1	<1
Ge	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
In	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
K	100	60	100	50	20	50	500	5	<1	<1	<1	3	120	100	<1
La	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Li	<.1	5	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	.4	<.1	.5
Mg	20	100	100	100	200	50	200	10	50	20	20	30	30	30	40
Mn	<10	<10	15	20	<10	20	10	<10	<10	<10	<10	<10	10	<10	10
Mo	<10	<10	<10	<10	50	50	<10	<10	<10	<10	<10	<10	<10	20	20
Na	75	20	100	50	18	75	125	30	<1	<1	<1	20	30	20	15
Ni	850	700	1000	1000	450	2000	900	40	50	20	50	375	5000	1500	1000
P	150	500	<100	500	<100	2500	800	100	<100	500	<100	500	<100	<100	<100
Pb	100	100	170	300	150	400	50	80	100	100	150	150	160	200	160
Pd	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Sb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Sc	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Si	20	<12	<12	<12	16	12	12	12	<12	<12	<12	16	12	<12	40
Sn	1.2	3	2	1.5	1.6	200	40	1.2	6	2	3	10	5	2	2
Sr	<20	<20	<20	<20	<20	30	<20	<20	<20	<20	<20	<20	<20	30	20
Te	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Ti	<10	<10	<10	<10	10	10	<10	<10	<10	<10	<10	<10	<10	<10	<10
V	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	-	-
Zn	<20	50	75	50	<20	<20	<20	<20	<20	<20	<20	25	<20	<20	<20
ppm															
Totals	1839	2727	2802	3410	1762	8007	4392	1055	1175	1438	1105	1938	6092	2690	2003

Note: All the values in Table IV are reported as microgram of Impurity per grams of plutonium (ppm).

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DISCUSSION

FLUORIDE ANALYSIS

Two ways of determining the fluoride concentration in the steam condensate were investigated: (1) titration of the fluoride with thorium nitrate, and (2) titration of the hydrogen fluoride with standard sodium hydroxide.

A titration of the fluoride at a pH of 3 was tried using standard thorium nitrate and xylenol orange as an indicator. The color of the solution changed from a yellow to a pink when excess thorium was available to form a complex with the indicator. However, the pink color was quickly removed from the solution by being absorbed on the thorium fluoride crystals, thereby making the exact end point rather difficult to discern. Results on prepared sodium fluoride solutions were low by an average difference of 0.15 mg for a fluoride concentration range of 2.90-5.80 mg. For many of the samples analyzed, plutonium was found in the condensate. Consequently, this method was discontinued since the plutonium formed a purple complex with xylenol orange indicator.

The simple acid base titration was complicated by the presence of plutonium in the condensate. To keep the plutonium from hydrolyzing during the titration, sodium citrate, which had previously been neutralized, was added to complex the plutonium. A previous study by Pflug and Miner⁽³⁾ reported sodium citrate as being a satisfactory complexing agent for plutonium when free acid determinations were made.

SOLUBILITY OF PLUTONIUM TETRAFLUORIDE SAMPLES

The evidence of soluble plutonium in the condensate suggested that the stream of hot steam was capable of dissolving some portion of the sample. Consequently, 1.0015 grams of sample No. 314 were pyrohydrolyzed and the steam condensate was checked for plutonium. Alpha counting indicated the presence of 3.5 mg of plutonium representing 0.35 percent of the sample.

For water solubility information on the tetrafluoride samples, 1-gram portions were leached at room temperature for approximately 16 hours (overnight) with 100 ml of water. After filtering the sample, the filtrate was diluted to 250 ml volume and was checked for plutonium by alpha counting procedures. The results are presented in Table V. The solubility of the samples in 14 N nitric acid was also carried out following the same procedure. The acid results are included in Table V. It is apparent from Table V that a small portion of the sample is water soluble. The water leaching information shows more consistency for the batch process, while the acid results show variations of a factor of two for both processes.

TABLE V
SUMMARY OF LEACHING INFORMATION

<u>Sample No.</u>	<u>Percent of Soluble Plutonium</u>		<u>Solubility of Pu in PuF₄ Samples</u>	
	<u>Water</u>	<u>Acid</u>	<u>Water</u>	<u>Acid</u>
Continuous Process				
739	1.64	9.50	0.087 g/l	0.501 g/l
764	2.45	9.20	0.129 "	0.488 "
774	1.80	10.50	0.095 "	0.554 "
776	1.82	5.00	0.096 "	0.264 "
779	0.87	5.50	0.035 "	0.290 "
Average	1.72	7.94	0.088 g/l	0.419 g/l
Batch Process				
555	2.95	47.50 ^a	0.156 g/l	2.504 g/l ^a
700	2.48	7.75	0.130 "	0.408 "
701	2.50	10.25	0.132 "	0.540 "
Average	2.64	9.00	0.139 g/l	0.474 g/l
Batch Process				
314	1.58	7.52	0.072 g/l	0.397 g/l
321	1.11	10.80	0.058 "	0.569 "
325	1.62	18.75	0.086 "	0.989 "
328	1.37	9.50	0.084 "	0.501 "
Average	1.42	11.64	0.075 g/l	0.614 g/l

^a Not used in calculating the average.

RECOVERY RATE FOR FLUORIDE

A study of the pyrohydrolysis rate was undertaken by titrating the steam condensate in 5-minute increments for 30 minutes. The major portion of the fluoride (99.7 percent) was recovered during the first 5 minutes. No fluoride was recovered after 15 minutes. The release of HF is rather rapid as the average time interval between sample

entry and the detection of HF in the steam condensate was 16.6 seconds. The minimum time interval was 16.3 seconds, while the maximum was 16.9 seconds.

PLUTONIUM ASSAY

Although the original purpose of this project was to eliminate the tedious task of converting the tetrafluoride to oxide by air oxidation, it became necessary to use this method for the plutonium assay. The leaching of the plutonium by the hot steam had not been anticipated.

The air oxidation of the tetrafluoride to oxide at elevated temperatures may be described by equations (2) and (3):

Since the air oxidation of the tetrafluoride is carried out in a small muffle, the successful completion of reaction (2) would depend upon the moisture content of the atmosphere in the muffle. The reaction described by (3) would not be expected to take place⁽⁴⁾ since it would necessitate a large positive free-energy change. Therefore, reaction (2) appears to be the logical way the conversion of tetrafluoride to oxide takes place within the muffle used for the analysis.

On several occasions, black spots were observed in the converted PuO_2 . C. E. Holley and others⁽⁵⁾, at Los Alamos, have observed black spots of indefinite composition when gelatinous peroxide was ignited to oxide. Drummond and Welch⁽⁶⁾ have reported the occurrence of black

spots in plutonium oxide formed from the air conversion of plutonium fluoride at elevated temperatures.

X-ray analysis identified these spots as PuO_2 , with traces of PuF_3 . It is difficult to explain the formation of the trifluoride using the conditions employed for the conversion of the tetrafluoride to oxide. A possible explanation is given by the reaction scheme offered by Dawson⁽⁷⁾ and his co-workers:

However, it is rather difficult to imagine this scheme taking place in an ordinary muffle furnace. The occurrence of the black spots was eliminated by keeping the sample weight below 350 mg and spreading the sample out to expose a maximum surface area.

The literature^(6,7) recommends heating of the plutonium oxide to at least 1000°C , or preferably to 1200°C , to obtain stoichiometric oxide. Several tetrafluoride samples were converted to oxide at 1000°C and 850°C . No significant differences were found in the plutonium assay and no significant differences in crystal structure were detected by X-ray. Unfortunately, the furnace used for the conversion had a maximum temperature range of 1000°C . Since no furnace was available for obtaining higher temperatures, no conversions were made at 1200°C .

Drummond and Welch report different plutonium-to-oxide ratios for plutonium oxide based on ignition temperatures and the original starting

material. The ratio for PuO_2 obtained at 870°C from the sulfate was 1-to-2.089, while for metal the ratio was 1-to-2.015. The ratios for PuO_2 prepared from metal and sulfate were 1-to-2.000 when the ignition temperature was raised to 1200°C . Although no specific data were given for oxide prepared from the tetrafluoride, reference was made to the fact that PuO_2 , formed at temperatures below 1180°C , would have a plutonium-to-oxygen ratio between 2.000 and 2.100. Consequently, the plutonium results in this report may be in error by 0 percent to 0.52 percent, since the gravimetric factor used in the determination was based on a 1-to-2.000 ratio.

GRAVIMETRIC CALCULATION FOR PLUTONIUM

Since the plutonium oxide formed contains some impurities which are also assumed to be oxides, it is necessary to correct for their presence before applying the gravimetric factor for $\text{PuO}_2 \rightarrow \text{Pu}$. The correction is made by determining the elemental impurities spectrographically and converting each value to its respective oxide value. The summation of the oxide values is applied according to equation (I), which is derived below:

$$(1) \quad \% \text{ Pu} = \frac{\text{grams of Pu}}{\text{grams of sample}} \times 100$$

$$(2) \quad \text{g of Pu} = 0.8820 \times \text{g of PuO}_2$$

$$(3) \quad \text{g of PuO}_2 = \text{g of muffled oxide} - \text{g of oxide impurities}$$

$$(4) \quad \text{g of oxide impurities} = \sum_{i=1}^n f_i g_i \text{ of metal imp.}$$

n = number of correctable impurities

f_i = gravimetric factor for i th impurity oxide

$$(5) \quad g_i \text{ of metal impurity} = (\text{ppm})_i \text{ of metal imp.} \times \text{grams of sample} \times \% \text{ Pu} \times 10^{-8}, \text{ where } (\text{ppm})_i = \text{parts metal impurity per million parts of Pu metal.}$$

$$\begin{array}{ccc} \text{(1) and (2)} & & \text{(3)} \\ \% \text{ Pu} = \frac{0.8820 \times \text{g of PuO}_2}{\text{g of sample}} \times 100 & = & \frac{0.8820 (\text{g of muffled oxide} - \text{g of oxide impurities})}{\text{g of sample}} \times 100 \end{array}$$

$$\text{(4)} \\ \% \text{ Pu} = \frac{0.8820 (\text{g of muffled oxide} - \sum_{i=1}^n f_i g_i \text{ of metal imp.})}{\text{g of sample}} \times 100$$

$$\begin{array}{c} \text{(5)} \\ \% \text{ Pu} = \\ \frac{0.8820 [\text{g of muffled oxide} - \sum_{i=1}^n f_i (\text{ppm})_i \text{ metal imp. (g of sample} \times \% \text{ Pu} \times 10^{-8})]}{\text{g of sample}} \times 100 \end{array}$$

$$\begin{array}{c} \% \text{ Pu} \times \text{g of sample} = \\ 0.8820 [\text{g of muffled oxide} - \sum_{i=1}^n f_i (\text{ppm})_i (\text{g of sample} \times \% \text{ Pu} \times 10^{-8})] \times 100 \end{array}$$

$$\begin{array}{c} \% \text{ Pu} \times \text{g of sample} = \\ 0.8820 (\text{g of muffled oxide} - \sum_{i=1}^n f_i (\text{ppm})_i \times 10^{-6} \times \text{g of sample} \times \% \text{ Pu} \times 0.8820) \end{array}$$

$$\% \text{ Pu} \times \text{g of sample} + \sum_{i=1}^n f_i (\text{ppm})_i \times 10^{-6} \times \text{g of sample} \times \% \text{ Pu} \times 0.8820 = 0.8820 (\text{g of muffled oxide})$$

$$\% \text{ Pu} \times \text{g of sample} (1 + \sum_{i=1}^n f_i (\text{ppm})_i \times 10^{-6} \times 0.8820) = 0.8820 (\text{g of muffled oxide})$$

$$\% \text{ Pu} = \frac{0.8820 \text{ (g of muffled oxide)}}{\text{g of sample} \left[1 + \sum_{i=1}^n f_i \text{ (ppm)}_i \times 10^{-6} \times 0.8820 \right]}$$

or

Equation I

$$\% \text{ Pu} = \frac{0.8820 \text{ (g of muffled oxide)}}{\text{g of sample} \left[1 + (\% \text{ of impurity oxides in PuO}_2 \times 10^{-2}) \right]}$$

IMPURITY ANALYSIS

Evidence of plutonium in the steam condensate suggested the possibility of the impurities leaching also. Consequently, an impurity analysis was made on the PuO_2 prepared by air conversion and also on the PuO_2 prepared by pyrohydrolysis. A comparison study was made on the results and, at the 95-percent confidence level, no significant differences between the averages for 37 elements were found using Student's "t" test as the test of significance.

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