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Chemistry - Transuranic Elements

A STUDY OF PLUTONIUM TRIFLUORIDE
PRECIPITATED FROM AQUEOUS SOLUTION

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A STUDY OF PLUTONIUM TRIFLUORIDE
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INTRODUCTION

In view of the increasing number of methods for determining plutonium in terms of weight rather than radioactivity, a need has arisen for a plutonium compound that can be used as a gravimetric standard. An easily prepared compound that dissolves readily in nitric acid is desirable. Wallman⁽⁸⁾ prepared a plutonium trifluoride of consistent composition that was dissolved by dilute nitric acid. The present study was made to determine the feasibility of using plutonium trifluoride as a plutonium standard. The preparation, composition, stability, solubility, and ignition of the compound are discussed, as are certain properties of the plutonium dioxide resulting from ignition of the trifluoride.

SUMMARY

Plutonium trifluoride precipitated from aqueous solution and dried at room temperature is of sufficiently reproducible composition to serve as a primary plutonium standard. On the basis of a limited number of analyses, preparations made by the most suitable technique were found to have a plutonium content of $78.5 \pm 0.2\%(\sigma_x)$.

The trifluoride, when dried at room temperature, has a water content of $2.3 \pm 0.3\%(\sigma_x)$ corresponding to the formula $\text{PuF}_3 \cdot 0.40 \text{ H}_2\text{O}$. The material undergoes slow hydrolysis to the oxide, but the composition can be considered constant for at least seven weeks. When dried at 200°C in vacuum, it loses weight but becomes hygroscopic so that the loss is regained on standing in air.

From the standpoint of ease of preparation and dissolution, the trifluoride appears to be satisfactory as a plutonium standard. Concentrations up to 15 g/l of Pu in 2 N nitric acid are readily prepared, and higher

concentrations are attainable. The plutonium dioxide formed by ignition of the trifluoride, while requiring an extra preparation step, has some advantages over the trifluoride as a plutonium standard in that it dissolves more easily, should be stable indefinitely, and has a definite and easily reproducible composition.

DISCUSSION

Properties of Plutonium Trifluoride

The properties of the plutonium trifluoride discussed are composition, stability, solubility, and ignition. The composition was obtained by plutonium, fluoride, and water determinations. The plutonium was determined by several methods. The fluoride analysis was by the pyrohydrolytic method and the water analysis by titration with Karl Fischer reagent. The stability of the material in air is discussed, as is its solubility in dilute acids. The ignition of the trifluoride in air is also described.

The plutonium trifluoride was prepared by reducing a plutonium(III-IV) chloride solution with sulfur dioxide, precipitating the trifluoride with hydrofluoric acid, washing with water, and drying with methanol and ether. A detailed description of the preparation is given later.

Composition

The composition of the plutonium fluoride was found to be constant under similar conditions of preparation. Small variations in precipitation conditions, such as concentration of plutonium, hydrochloric and hydrofluoric acids, order of adding the plutonium and hydrofluoric acid, and length of digestion period had no apparent effect on the composition. The solvent drying step and a subsequent drying period were important in assuring a constant water content. No effect on the composition was noted from variously storing the material for periods of days in air, nitrogen, desiccator, or vacuum.

The data from analysis of the several preparations are shown in Table I. Plutonium was analyzed by four different techniques, and since the gravimetric method is considered most reliable, no attempt was made to search for or correct for biases between them. Analyses by each separate method indicate a uniform composition of the material; those by the radiochemical assay, which employs micro samples, indicate the homogeneous nature of the preparations. Both the plutonium and fluoride results on samples dried at 200°C in vacuum indicate a change of composition, although results for samples dried in vacuum at 60 and 120°C indicate no change.

TABLE I
SUMMARY OF ANALYTICAL RESULTS

Sample	Drying Temp.	Pu				F	H ₂ O
		Radio Assay	X-Ray Photo-metric	Coulo-metric	Gravi-metric	Pyro-hydrolysis	Karl Fischer
1	200°C			77.9%	78.3%(3)	16.2%	
2						16.3	
3	120°C			77.0	76.6 (3)	17.9	
4	60°C	75.7%		77.8	77.3 (3)	17.4	
5	25°C	76.1					
6		76.0		76.5			
7			77.2%	77.1			
8					76.4 (3)	17.9	2.1%(1)
9						17.3	2.1 (2)
10(5)			76.2	74.8	78.3		2.5
11(4)					78.7		2.2
12(6)			77.3		78.3	17.4	2.6
13			77.6		78.6	17.7	1.8

- [illegible]

The first four gravimetric plutonium results in Table I were obtained by weighing the oxide resulting from the pyrohydrolytic fluoride determination. Some loss of plutonium was noted during the hydrolysis, and it was subsequently observed that preparations made by adding plutonium to hydrofluoric acid yielded a fluffier precipitate than those obtained by the reverse precipitation. As a consequence, samples 10 to 13, which were precipitated in the former manner, were ignited to oxide at a temperature of 500-600°C in the presence of a very slow moving stream of moist air. No plutonium loss was observed. Hence, these analyses are considered most reliable.

The fluoride content of the material was determined by the pyrohydrolytic method,⁽⁹⁾ in which steam at about 1000°C is used to hydrolyze the fluoride according to the reaction $\text{PuF}_3 + 2\text{H}_2\text{O} \longrightarrow \text{PuO}_2 + 3\text{HF} + 1/2 \text{H}_2$. The hydrofluoric acid released is titrated with standard base to effect the determination. The samples that had been dried at 200°C exhibited a lower fluoride content. The remainder had an average fluoride value of $17.6 \pm 0.3\%$ (σ_x), which is about 1% lower than the theoretical value (18.7%) calculated for a plutonium content of 78.5% and assuming an F to Pu ratio of 3:1. Precipitates made by adding plutonium to fluoride and by the reverse procedure showed no difference in final fluoride content.

It is interesting to note that two samples which had been heated to 200°C under vacuum had fluoride values of 16.2% and 16.3%, the lower fluoride content probably indicating slight hydrolysis. The former sample, after being heated to 60°C, stood in air for four weeks before being heated to 200°C. The appearance of the material was changed after the 200°C heating, the color being grey with a slight oxide-like, yellow cast instead of dark purple. In view of the extended treatment, it is surprising that the oxidation was not greater than that observed. The latter sample did not change in appearance on being heated at 200°C but stood in air for six weeks before the analysis was made.

The solvent-dried plutonium trifluoride was found to have $0.40 \pm 0.05(\sigma_x)$ moles of water per mole of compound. One investigator has reported finding about three-quarters mole of water in plutonium trifluoride precipitated from aqueous solution.⁽¹⁾ Another reported loss of weight on heating the trifluoride in vacuum at 200-300°C of 2.21-3.65%, which is equivalent to 0.38-0.63 moles of water.⁽⁸⁾ In the present study two preparations showed weight losses of 2.1% when heated in vacuum, one to 120°C and the other to 200°C. This does not necessarily represent the complete weight loss on heating, since the material dried at elevated temperatures is extremely hygroscopic, and some moisture could have been picked up before the material was reweighed. Direct water determinations with Karl Fischer reagent gave an average of $2.3 \pm 0.3\%(\sigma_x)$ water for four preparations. The solid was suspended in methanol and titrated with Karl Fischer reagent to a "deadstop" endpoint.⁽⁵⁾ The water was readily removed from the solid in the methanol system, except from the larger aggregates as indicated by a slowing of the titration near the endpoint.

Table II summarizes the results and some calculations for the most satisfactory preparations and analyses. The low fluoride content indicates the presence of some plutonium oxide, but the results from the several analyses indicate that the selected method of preparation yields a constant quantity of oxide so that the plutonium content can be accepted as reproducible.

TABLE II
CORRELATION OF WATER AND PLUTONIUM VALUES

<u>Sample</u>	<u>Pu Found</u>	<u>H₂O Found</u>	<u>F Found</u>	<u>F Calc. (1)</u>	<u>Total</u>
10	78.3	2.5		18.7	99.5
11 ⁽²⁾	78.7	2.2		18.8	99.7
12	78.3	2.6	17.4		98.3
				18.7	99.6
13	78.6	1.8	17.7		98.1
				18.7	99.1
Average	78.5	2.3	17.6		98.4
				18.7	99.5

(1) Assuming F/Pu = 3:1.

(2) Same preparation as 10, analysis 6 weeks later.

Stability

The plutonium trifluoride prepared in this study was found to be stable for at least 6 - 7 weeks, with only slight hydrolysis apparent in this length of time. One preparation showed Pu and H₂O values after five days of 78.3% and 2.5%, respectively. After seven weeks, the values were 78.7% and 2.2%, respectively. Another preparation had a fluoride value of 17.3% after standing in air six weeks. No analyses were made on material more than seven weeks old, although color changes indicated that slow hydrolysis occurs. Material that had been standing in air for 6 - 8 months had turned from dark purple to grey and had a slight yellowish cast. Another sample, after standing twelve months, had a definite yellow-green cast of the oxide.

In regard to the water content, it is interesting to note that a preparation that was not efficiently solvent-dried showed a water content of 6.4% the first day after preparation, 3.3% after four days, 2.5% after five days, and 2.2% after seven weeks. A water content of about 2.3% seemed to be stable for several weeks in the atmosphere of this laboratory, where the relative humidity ranged from 25 - 50%.

Solubility

Plutonium trifluoride is considered difficult to dissolve,⁽⁶⁾ a recommended method being sulfuric acid fuming. However, Wallman⁽⁸⁾ prepared a plutonium trifluoride precipitated from aqueous solution which dissolved readily in dilute nitric acid; he reported plutonium concentrations of about 0.2 g/l. The material used in this study was prepared somewhat similarly to that of Wallman and was also found to be dissolved by dilute nitric acid, with plutonium solutions up to 15 g/l being prepared in this way. Dilute hydrochloric acid also dissolved the trifluoride.

In low concentrations (< 5 g/l Pu) the trifluoride dissolves in 15 - 30 minutes in 2 N HNO_3 , either cold or with gentle heating. In concentrations of 5 - 15 g/l of plutonium the dissolution takes place more slowly, usually requiring 1 - 3 hours with gentle refluxing. The material dissolves very slowly at plutonium concentrations greater than 15 g/l. For these concentrations it is quicker to dissolve the material in a larger volume of acid and evaporate to the desired plutonium concentration.

During the dissolution of PuF_3 in dilute HNO_3 , color changes indicate that two intermediate compounds are formed, particularly at the higher plutonium concentrations. One is a tan-to-white compound, similar in appearance to plutonium tetrafluoride, which dissolves at about the same rate as the trifluoride. The other, a reddish brown compound, appears less frequently and is more difficult to dissolve. No attempt has been made to isolate or further identify the intermediate compounds.

Ignition

It has been reported that plutonium trifluoride is converted to plutonium dioxide at 300-350°C in air.⁽⁴⁾ The reaction is presumed to be that of PuF_3 and H_2O as in the equation above since it has been shown that dry oxygen reacts with PuF_3 to give $\text{PuF}_4 + \text{PuO}_2$.⁽²⁾ In this study the trifluoride (60-170 mg) was heated in air in a platinum boat for one to four hours at 400-600°C and 30 - 50 minutes at 800°C. Two samples were heated at 250-300°C for one hour before the temperature was raised to the 400°C region.

The resulting oxide was a finely divided, yellow-green powder shown by x-ray diffraction methods to be PuO_2 (at least 90% or possibly 95% pure). It is believed that the conversion of the trifluoride to the oxide was complete. One sample of oxide was moistened with 6 N HNO_3 and reignited; no additional weight loss occurred.

Color changes of the material during heating were roughly as follows: room temperature, purple, 250-300°C, greyish purple; 300-400°C, yellow-green; 400-500°C, reddish brown. The reddish brown material was stable only at the higher temperatures and changed quickly to yellow-green on cooling. Some properties of the oxide are described below.

Properties of the Dioxide

The yellow-green plutonium dioxide obtained by ignition of the trifluoride is a free-flowing powder which is readily dissolved in strong acid. The ease of dissolution is surprising, particularly in view of the temperature reached during ignition, as plutonium dioxide has frequently been reported to be very refractory,^(3,10) requiring long fuming,⁽⁷⁾ fusion,⁽⁶⁾ or heating with acid in a sealed tube⁽⁷⁾ to dissolve it. The very small particle size, estimated to be 10^{-5} to 10^{-6} cm*, may explain the ready dissolution of this material. A 100 mg portion dissolved in 10 ml of concentrated

*Estimated from the x-ray diffraction line broadening.

HNO_3 - 0.1 N HF in five minutes with gentle heating. It is likely that a smaller volume and possibly a lower concentration of acid would also effect dissolution. The dioxide dissolves much more slowly at room temperature; a 120 mg sample in 8 ml of the mixed acid required two hours for the majority of the sample to be dissolved, and about four hours for the larger aggregates.

The ease of dissolution of plutonium dioxide prepared in this way, along with its expected qualities of consistent composition and long stability, make it a practical plutonium standard.

Preparation of Plutonium Trifluoride

The source of plutonium used to prepare the trifluoride was metal dissolved in hydrochloric acid. One-tenth to one gram of plutonium (5-85 g/l) in 2-3 N HCl was reduced to the +3 state by bubbling SO_2 through the solution. The reduced plutonium was then added slowly to a hydrofluoric acid solution such that the final concentration of HF was 2-3 N. After thorough stirring, the lavender precipitate was allowed to digest 15-60 minutes, centrifuged, and washed twice with water. If peptization occurred on the second wash, a little methanol was added before centrifuging. Usually peptization did not occur unless more than two washes were made. The precipitate was then washed twice with methanol. Peptization occurred occasionally on the second methanol wash, in which case a little diethyl ether was added. The precipitate was transferred to a fine-porosity, sintered-glass filter with a 50-50 mixture of ether and alcohol. If too much ether is used, the precipitate clings together in a sticky mass and is difficult to transfer. Too much alcohol in the mixture slows the filtering. The precipitate was then washed thoroughly with ether and air was drawn through the funnel for 15-20 minutes. The material was transferred to a platinum crucible and stored in a desiccator charged with Drierite for several hours or overnight. Any lumps due to insufficient removal of the ether were readily powdered with a glass rod after a few hours.

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