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**THE DETERMINATION OF FLUORIDE
IN PLUTONIUM FLUORIDES**

by

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Analytical Chemistry Division

November 1957

**E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
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ABSTRACT

The Willard-Winter distillation was adapted to the determination of fluoride in plutonium fluorides. Fluoride was distilled from samples in 12M sulfuric acid, and the distillate was then titrated to a visual end point with a standard solution of thorium nitrate. In the analysis of plutonium trifluoride the average recovery of fluoride was 98.6 per cent of theoretical, and the standard deviation of the results was 1.3 relative per cent.

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THE DETERMINATION OF FLUORIDE IN PLUTONIUM FLUORIDES

INTRODUCTION

In a study of the precipitation of plutonium trifluoride from aqueous solutions, an analysis was required for fluoride in precipitates prepared under different conditions. A knowledge of the fluoride content was important in the identification of plutonium trifluoride in samples that might contain plutonium tetrafluoride, or hydrates of these compounds.

A precision of two per cent was considered adequate for the fluoride analysis. The objective of the work reported here was to provide a simple analytical method that requires only conventional laboratory equipment and that presents no unusual hazards in the analysis of relatively large amounts of plutonium.

Lee, Edgerton, and Kelley⁽¹⁾ used pyrohydrolysis for the separation of fluoride and applied this method to the determination of fluoride in uranium and plutonium fluorides. Special platinum or nickel equipment was required for the pyrohydrolysis, and operation of the furnace at high temperatures required a special gloved box to contain the plutonium. The Willard-Winter⁽²⁾ steam distillation has been applied to the analysis of fluoride in many inorganic fluoride compounds. Conventional glass equipment is used in this procedure, and the method is readily adaptable to radioactive samples.

To use steam distillation for the analysis of plutonium trifluoride, it was necessary to show that fluoride was distilled quantitatively from plutonium trifluoride and plutonium tetrafluoride.

SUMMARY

The fluoride content of plutonium fluorides was determined by distillation of the fluoride from aqueous sulfuric acid followed by titration of fluoride in the distillate with thorium nitrate. An average recovery of 98.6% was obtained in the analysis of plutonium trifluoride, and the standard deviation of the data for repeated analyses was 1.3%.

Fluosilicic acid was steam distilled from the sample in 12M sulfuric acid at the boiling point, and the distillate was then titrated to a visual end point with a thorium nitrate solution. The method requires only standard laboratory equipment and conventional gloved boxes.

DISCUSSION

In the Willard-Winter distillation, fluoride is distilled from aqueous sulfuric acid as fluosilicic acid. Fluoride in the distillate may then be determined by volumetric titration or by

colorimetric methods. Titration with a standard thorium nitrate solution was chosen for the analysis of the distillate in this work.

Conditions were established for the quantitative distillation of fluoride from plutonium compounds by studying the effect of acid concentration and the rate of distillation of fluoride. A detailed analytical procedure is given in the Appendix.

APPARATUS

The distillation apparatus shown in Figure 1 was similar to that described by Smith and Parks⁽³⁾. The distillation flask was coated on the bottom of the inside surface with powdered "Pyrex" glass to facilitate the reaction of the fluoride ions with silica.

Titration of Fluoride

The stoichiometry for the titration of fluoride with thorium nitrate depends on the indicator, the pH at the equivalence point, and the concentration of fluoride in the solution.

Alizarin Red S was used as the indicator in the titration. The solution was adjusted to a pH of 3.05 with dilute perchloric acid or sodium hydroxide, and a buffer solution, prepared from monochloroacetic acid and sodium hydroxide, was added to maintain the pH during the titration. To determine the stoichiometry for the titration, a standard curve was prepared by titrating different amounts of fluoride contained in 100-ml volumes of solution. Data for a typical standardization curve for a solution of thorium nitrate are given in the following table, and the curve is plotted in Figure 2.

TITRATION OF FLUORIDE WITH THORIUM NITRATE

<u>Fluoride, mg</u>	<u>Thorium Nitrate Solution, ml</u>
3.80	5.40
1.90	2.90
1.52	2.46
1.15	1.90
0.75	1.42
0.38	0.87

The precision for the titration of 1 to 4 mg of fluoride was 2.0%.

Distillation of Fluoride from Plutonium Trifluoride

The effect of acid concentration on the recovery of fluoride from plutonium fluoride was studied by distilling fluoride from 7M and 12M sulfuric acid. For distillation from 7M acid the temperature was

about 120°C, and from 12M acid the temperature was about 150°C. A total of 250 ml of distillate was collected in all runs, and the fluoride content was determined by titration with a standard thorium nitrate solution.

The recovery of fluoride was quantitative for both concentrations of acid. Since distillation from 12M acid gave a better precision for the subsequent titration of fluoride, this concentration of acid was chosen for the analytical method.

The rate of distillation of fluoride from 12M acid was determined by distilling the fluoride from 20-mg samples of PuF₃ and by analyzing successive 50-ml fractions of the distillate. The data given in the following table show that the initial rate of distillation varied over a wide range. In each case distillation of fluoride was complete after collection of 250 ml of distillate.

RATE OF DISTILLATION OF FLUORIDE FROM 12M SULFURIC ACID


<u>Fraction Number</u> (50 ml Volume)	<u>Fluoride Content, % of Total Theoretical</u>	
	<u>Run #1</u>	<u>Run #2</u>
1	72.3	45.0
2	22.7	36.3
3	3.3	12.1
4	1.0	3.4
5	0.8	2.4
6	0.0	0.0
7	0.0	0.0
8	0.0	0.0
9	0.0	0.0
TOTAL	100.1	99.2

Experimental Results

The precision and accuracy of the distillation method were determined by repeated analyses of plutonium trifluoride. Two samples of plutonium tetrafluoride were also analyzed to test the distillation of fluoride from the tetravalent plutonium compound. The plutonium compounds were prepared by precipitation from aqueous solution. Analyses for plutonium, water, and suspected contaminants indicated a sufficient degree of purity for this study.

All analyses were made by the procedure outlined in the Appendix with results as summarized in the following table. The average recovery of fluoride from 20-mg samples of plutonium trifluoride was 98.6 per cent, and the standard deviation of the results was 1.3 relative per cent. Fluoride was recovered quantitatively from plutonium tetrafluoride.

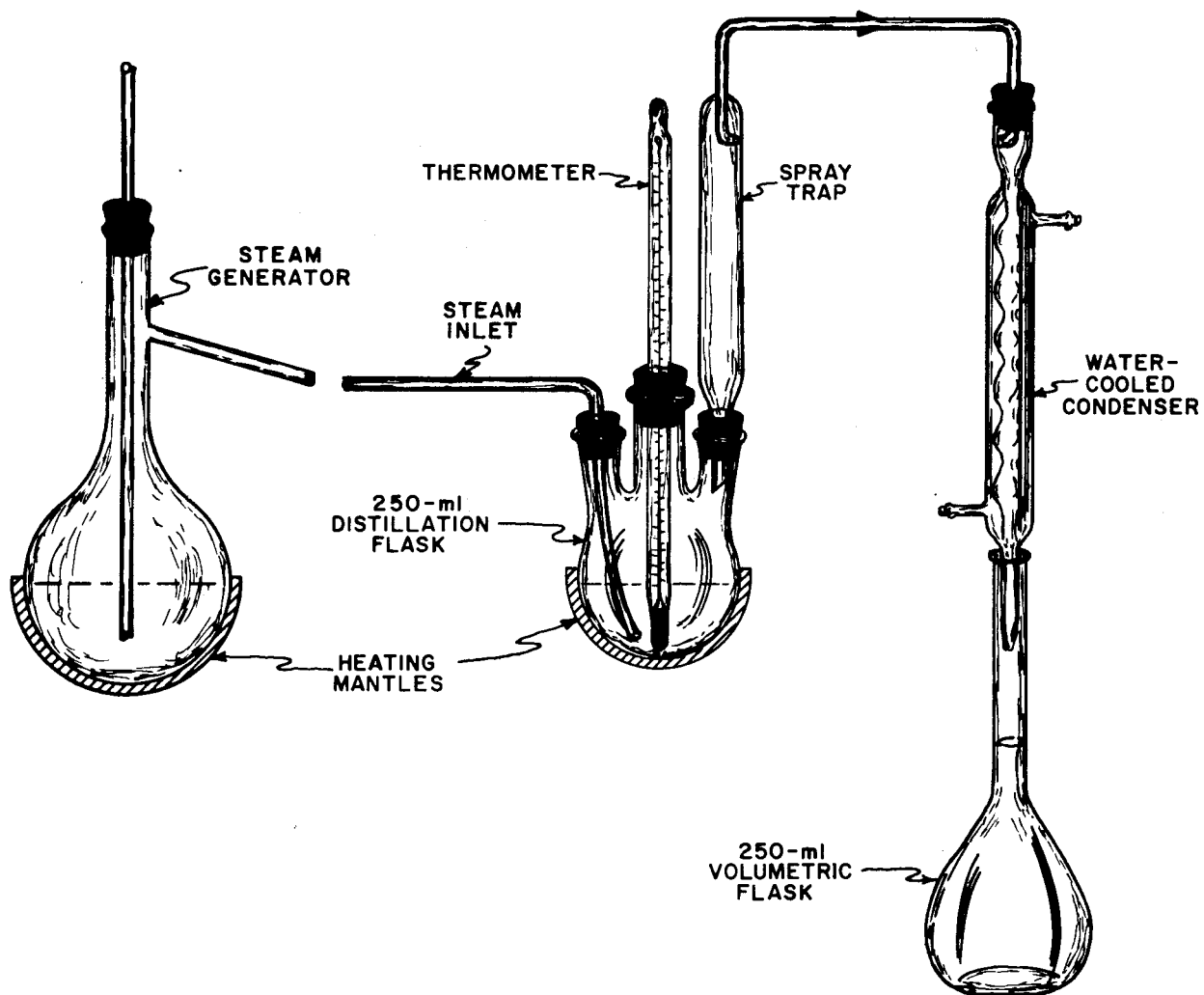
<u>Sample</u>	<u>Number of Determinations</u>	<u>Avg. Fluoride Found, % of Theoretical</u>	<u>Standard Deviation, Relative %</u>
PuF ₃	8	98.6	1.3
PuF ₄	3	99.7	-
PuF ₄ ·2.5H ₂ O	1	101.4	-


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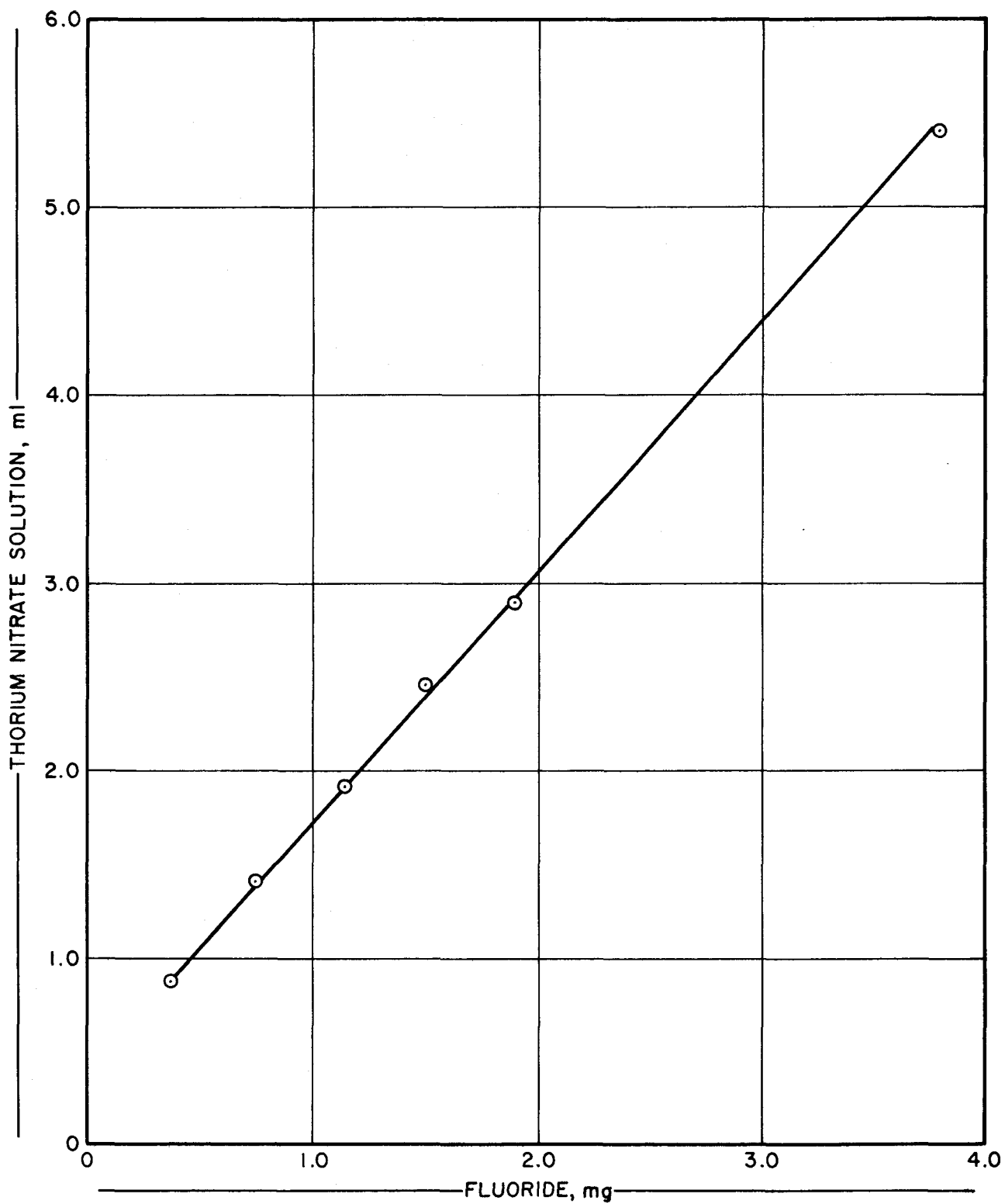
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FIGURE 1



DISTILLATION APPARATUS

FIGURE 2



STANDARDIZATION CURVE FOR TITRATION OF FLUORIDE

APPENDIX

DETAILED PROCEDURE FOR ANALYSIS OF FLUORIDE

Reagents

- Standard 0.02M sodium fluoride in distilled water
- 0.01M thorium nitrate in distilled water
- 0.1% solution of Alizarin Red S in distilled water
- 1% solution of perchloric acid
- Buffer solution, pH 3.05- 1M monochloroacetic acid, approximately 1M sodium monochloroacetate

Standardization of Thorium Nitrate Solution

1. Take aliquots of the standard sodium fluoride solution of 1, 3, 5, 7, 10, and 15 ml.
2. Dilute each aliquot to 100 ml with distilled water, and add 0.5 ml of Alizarin Red S solution.
3. Adjust the pH to 3.05 with one per cent perchloric acid and add 5.0 ml of buffer solution.
4. Titrate the solutions to the pink end point with the thorium nitrate solution.
5. Determine the titration blank by titrating a solution that contains all the reagents. Titrate to the same end point used in the titration of fluoride.
6. Calculate the net volume of thorium solution required to titrate each aliquot of the standard fluoride solution. Prepare a standard curve for the thorium nitrate solution by plotting the mg of fluoride versus the net ml of thorium solution.

Analysis of Samples

Samples of plutonium fluoride should be weighed and distilled in suitable gloved boxes. The distillate may be removed from the gloved box and titrated in a laboratory hood, if proper precaution is used for work with low levels of plutonium. Normal precautions should be taken in handling solutions of sulfuric acid.

1. Weigh a sample of plutonium fluoride to yield 4 to 5 mg of fluoride.
2. Add the sample to 125 ml of 12M sulfuric acid in the distillation flask, and connect the condenser.
3. Heat the flask to 135°C, and open the valve to admit steam to the distillation flask.

4. Adjust the steam rate so that the rate of distillation is about 2 ml per minute. Maintain the temperature in the distillation flask at $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$ by adjusting the heating unit.

5. Continue the distillation until almost 250 ml of distillate are collected. Adjust the volume of the distillate to exactly 250 ml, and remove two 100-ml aliquots for titration.

6. After the distillation equipment has cooled, rinse the flask and condenser with distilled water and pass steam through the equipment for 15 minutes prior to the analysis of a new sample. Under these conditions the distillation blank is negligible.

7. Titrate the 100-ml aliquots by the procedure used for the standardization of the thorium nitrate solution.

8. Read from the standard curve the mg of fluoride in each aliquot.

9. Calculate the per cent fluoride in the sample:

$$\% \text{ Fluoride} = \left(\frac{\text{mg fluoride in aliquot}}{\text{sample weight, mg}} \right) \times 2.5 \times 100$$