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TECHNOLOGY - PLUTONIUM

A.E.C. RESEARCH AND DEVELOPMENT REPORT

THE DETERMINATION OF FLUORIDE IN PLUTONIUM METAL BY THORIUM TITRATION

BY

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SEPARATIONS SECTION
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MAY 4, 1954

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Process Sub-Section

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THE DETERMINATION OF FLUORIDE IN PLUTONIUM METAL BY THORIUM TITRATION

INTRODUCTION

The need for an improved analysis for micro-amounts of fluoride in plutonium metal led to the examination of a Los Alamos method[1] on the development of a titrimetric method for fluoride. The method involves dissolution of the metal in dilute sulfuric acid, addition of concentrated sulfuric acid to precipitate most of the plutonium as (III) sulfate, and steam distillation of the supernatant to separate the fluoride. The distillate is then titrated with thorium nitrate, using a Gilmont buret (Emil Greiner Co.) equipped with a reagent reservoir. The distillation and titration equipment was designed to allow rapid analysis of large numbers of samples under routine control conditions.

EXPERIMENTAL

Samples of plutonium metal turnings were weighed in 200 mg amounts, and were dissolved in 1.5 ml of 3 N sulfuric acid, using a 15 ml centrifuge cone. Dissolution was complete in most cases within 30 minutes. (Samples dissolved routinely at a later date were consistently dissolved in less than 15 minutes.)

At a normality of 5, the reaction rate was more rapid, but, due to the higher concentration of sulfate, in many cases plutonium sulfate would crystallize out on the undissolved portion of metal.

To indicate the amount of fluoride loss if appreciable amounts of sample remain undissolved, three different 200 mg portions of a metal sample were incompletely dissolved. The solutions were separated from the residues, and the fluoride was distilled from the residues. The remaining supernatants were treated with concentrated sulfuric acid to separate the plutonium, and the fluoride was then distilled from both the supernate and the plutonium sulfate crystals. The results of the nine titrations, corrected for blank distallation, appear in Table I.

[redacted]

TABLE I

DISTRIBUTION OF FLUORIDE IN ALL COMPONENTS OF A SAMPLE

Microliters of Thorium Nitrate (Corrected)

Run No.	Solutions	Residues	Salts	Total
1	6	6	1	13
2	8	8	1	17
3	3	10	2	15

The data of Table I indicate that fluoride is lost if undissolved portions of sample are discarded. Using 3N sulfuric acid, in nearly all cases dissolution is complete. In those cases where it is not complete, the residue is added to the still along with the supernatant in order to quantitatively recover the fluoride present in the sample.

The separation of the plutonium from the fluoride was best obtained by addition of 1.5 ml of concentrated sulfuric acid, and centrifugation for two minutes.

The steam source was adjusted to distill water at the rate of 1.5 ml per minute, and the supernatant was admitted to the distillation flask. Twenty-five ml of distillate were collected and transferred to a 30 ml beaker. A 3.2 pH buffer of half-neutralized monochloroacetic acid and a thorium indicator were added, and the solution titrated with 0.001 M thorium nitrate.

A statistical study was made of indicators applicable to the acid buffered thorium fluoride titration[2,3]. There were several two color indicators that appeared satisfactory. Three of these were tested for sensitivity and reproducibility in the range of 0-10 μg fluoride. Sixteen standard solutions were titrated at a pH of 3.05 with 0.001 M thorium nitrate, with each of the three indicators. The results were interpreted with the aid of a regression analysis, using μg F^- as the

independent variable and μl thorium as dependent. The most favorable titer per μg F^- was obtained with chrome azurol-S, and this system also gives the best reproducibility. The only disadvantage that could be found in this indicator is a nonlinearity when extending the range to much larger amounts of fluoride. For applications of this type alizarin red-S was found to be more linear. Data applicable to the present application only are included in the table below.

TABLE II

	Indicator	Buffer	Slope
Name	Amount (mg)	Amount (mg)	μl Thorium μg F^-
Purpurin Sulfonate	0.075	23.62	15.3
Alizarin Red-S	0.100	23.62	21.2
Chrome Azurol-S	0.20	11.35	26.7*

Ratio of Variance	[Due to Regression]	[About Regression]
Purpurin Sulfonate	600.59	0.07021 = 8,554
Alizarin Red-S	1150.65	0.07785 = 14,780
Chrome Azurol-S	1835.92	0.08928 = 20,564*

*Best indicator for slope and for reproducibility.

Some batches of the half-neutralized monochloroacetic acid were found to affect the end point of the titration. The sharpness of the end point was lost and blank titrations required too much thorium. This was overcome by using sodium hydroxide that had not been exposed to the air excessively.

A study was made to determine the precision of the titration in the presence and absence of plutonium[4]. The first stock solution contained no plutonium and 10 mg fluoride/liter. The average found in a series of 15 titrations of 25 ml aliquots was 7.7 μl thorium, and the

precision on the 95% confidence level was ± 3.4 μl. The second stock solution contained 2 mg fluoride/liter and no plutonium. In this case the average titer was 2.9 μl and the precision ± 3.3 μl. The third stock solution contained about 28 μg fluoride/liter and 1.0×10^{-5} grams plutonium/liter. In this case the average titration was 17.9 μl and the precision was ± 4.5 μl, indicating this amount of plutonium will affect the precision somewhat.

CONCLUSIONS

A titrimetric method for the determination of fluoride in plutonium has been described, which is capable of detecting as little as one part per million fluoride with a precision of ± 0.65 ppm. The distillation equipment is designed for rapid analysis combined with safety and control of plutonium contamination, and is capable of recovering 87% or more of the fluoride content.

A series of 11 determinations was made on one sample to determine the precision of the complete analysis. The recovery of fluoride was determined by adding 1.0 μg of fluoride to four of the determinations. The results of this study are tabulated in Table III.

TABLE III

PRECISION AND ACCURACY STUDY ON DETERMINING FLUORIDE BY THORIUM TITRATION

Portion of sample	Fluoride Found (μg)	Fluoride Recovered from Spike (μg)
1	0.338	
2	0.236	
3	0.169	
4	0.270	
5	0.203	
6	0.338	
7	0.203	
Avg	0.251	
8 (1.0 μg F^- added)	1.114	0.863
9 " " "	1.249	0.998
10 " " "	1.013	0.762
11 " " "	1.114	0.863
	Avg	0.872 μg

Calculations from the data on portions 1 through 7 of Table III show the precision at the 95% confidence limits with which results for fluoride can be expected to be reproduced on metal samples determined by the method outlined in the procedure is ± 0.13 μg. No figures to give the accuracy of the method can be furnished because no standard fluoride-free plutonium metal samples are available. The recovery of the standard fluoride solution averaged 87%. The average analysis time required when analyzing a number of samples simultaneously is forty minutes. The equipment and techniques described are adopted for rapid analysis under routine control conditions.

W. S. Ferguson — D. M. Newell

WSF:DMN:ms

REFERENCES

1. Bergstrasser, K. S., Microdetermination of Fluoride in Plutonium Metal, Los Alamos Scientific Laboratory, Document LA-1369 (1952) (Secret).

2. Willard, H , Indicators for Titration of Fluoride with Thorium, Analytical Chemistry, 22, 1190 (1950).

3. Newell, D. M., Hanford Works Secret Notebook, HW-4675-T.

4. Ferguson, W. S., Hanford Works Secret Notebook, HW-4676-T.

APPENDIX

Special Apparatus

Drawings of the functional parts of the still, steam generator, and condenser are given in Figures 1, 2, 3 respectively. Detailed working drawings are available as Hanford Drawing No. SK-2-1580. The assembly of the complete distillation unit is shown in Figure 4, and Figure 5 is a photograph of the titration assembly. The still design features a 19 mm sample part for ease of transferring samples into the still. Provision for emptying the still is made by vacuum through a sidearm off the steam inlet line. The heating element of the two liter steam generating flask consists of a Chromel "A" coil which is immersed in the water. The outer jacket of the distillation flask contains s-tetrachloroethane (B. P. 145° C.), which is ideal for distillation of hydrofluoric acid and fluosilicic acid.

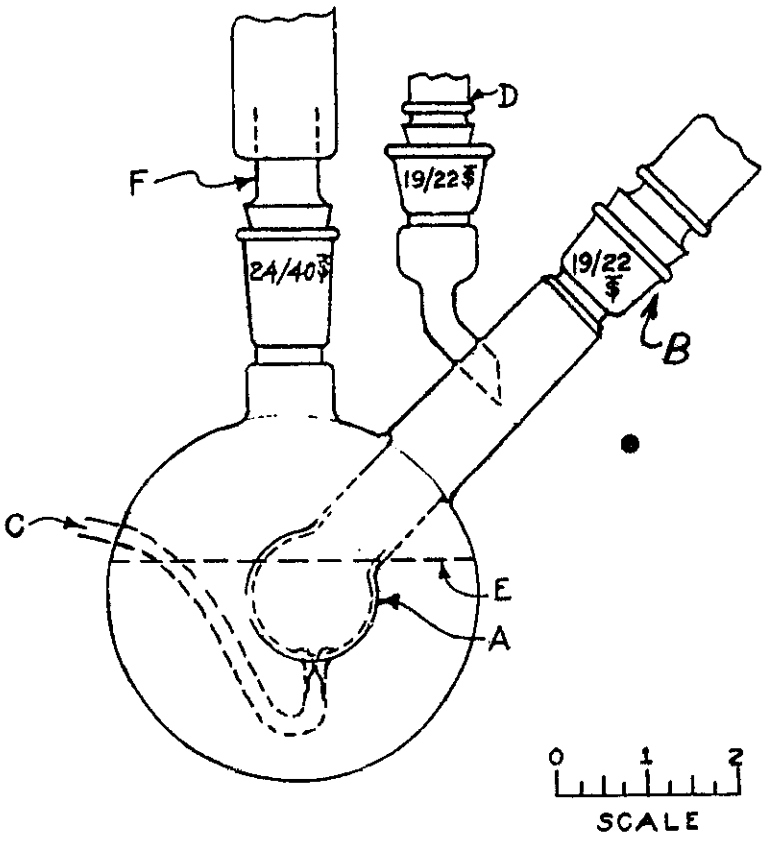

FIGURE 1
FLUORIDE STILL

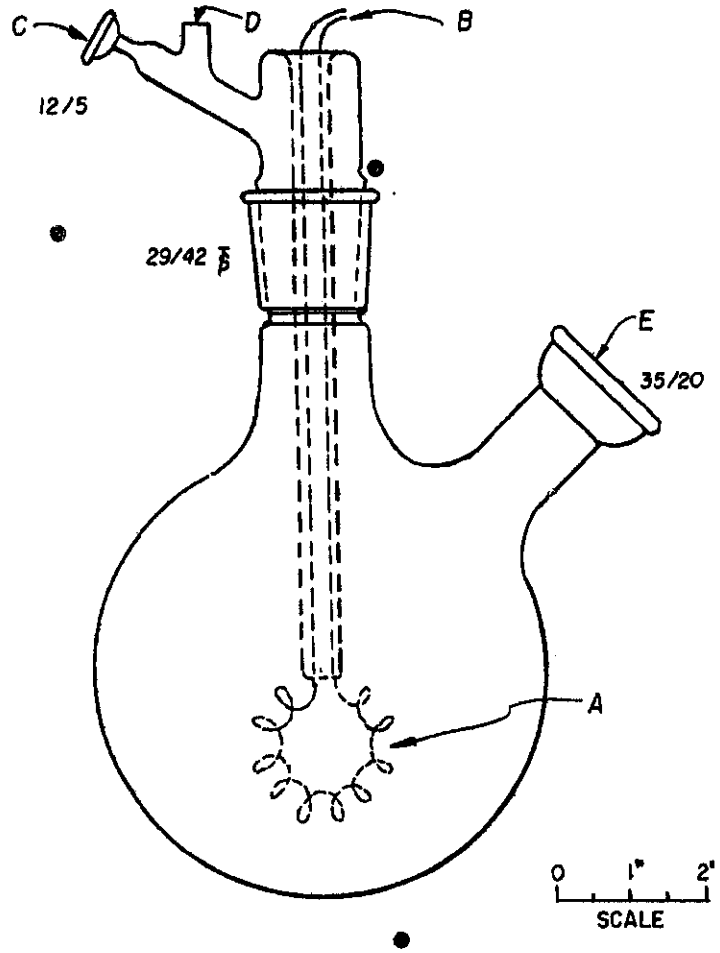

FIGURE 2

STEAM GENERATOR

A. Resistance heating coil.
B. Copper conductor leads to coil.
C. Steam outlet.
D. Sidearm to pressure release tube.
E. Entrance port for water.

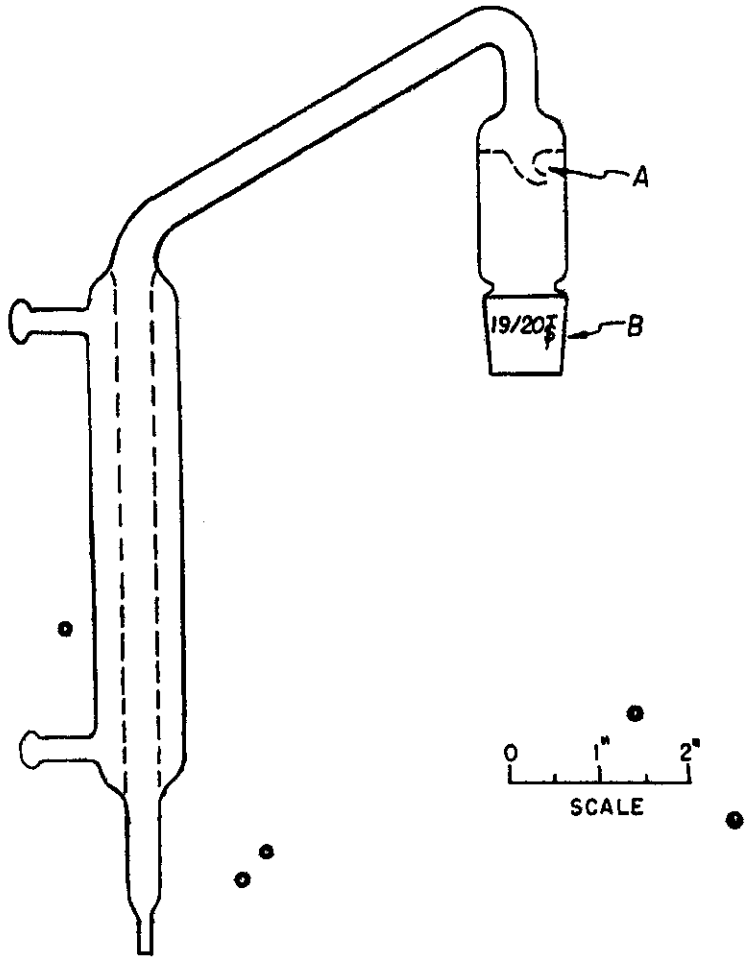

FIGURE 3

STILL CONDENSER

A. Spray trap.
B. Joint for connection to still.

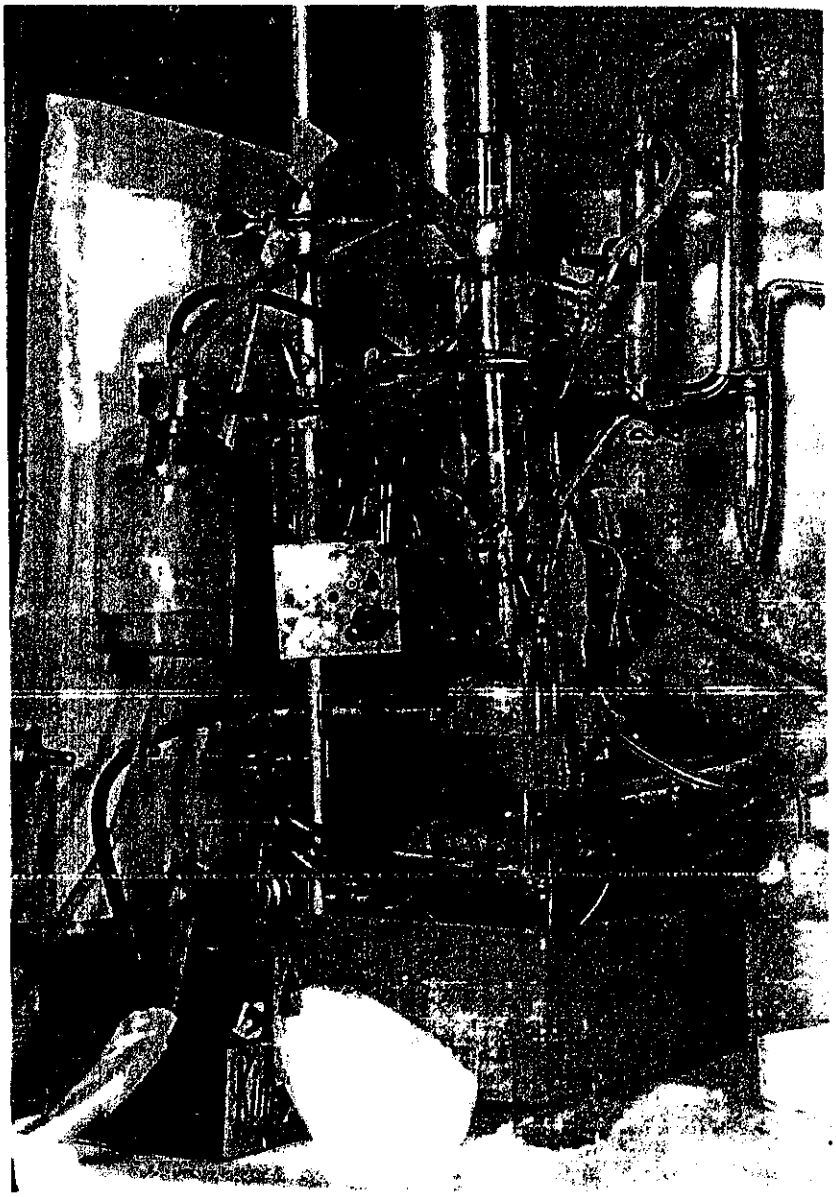

FIGURE 4
DISTILLATION ASSEMBLY

AEC-GE-RICHLAND, WASH.

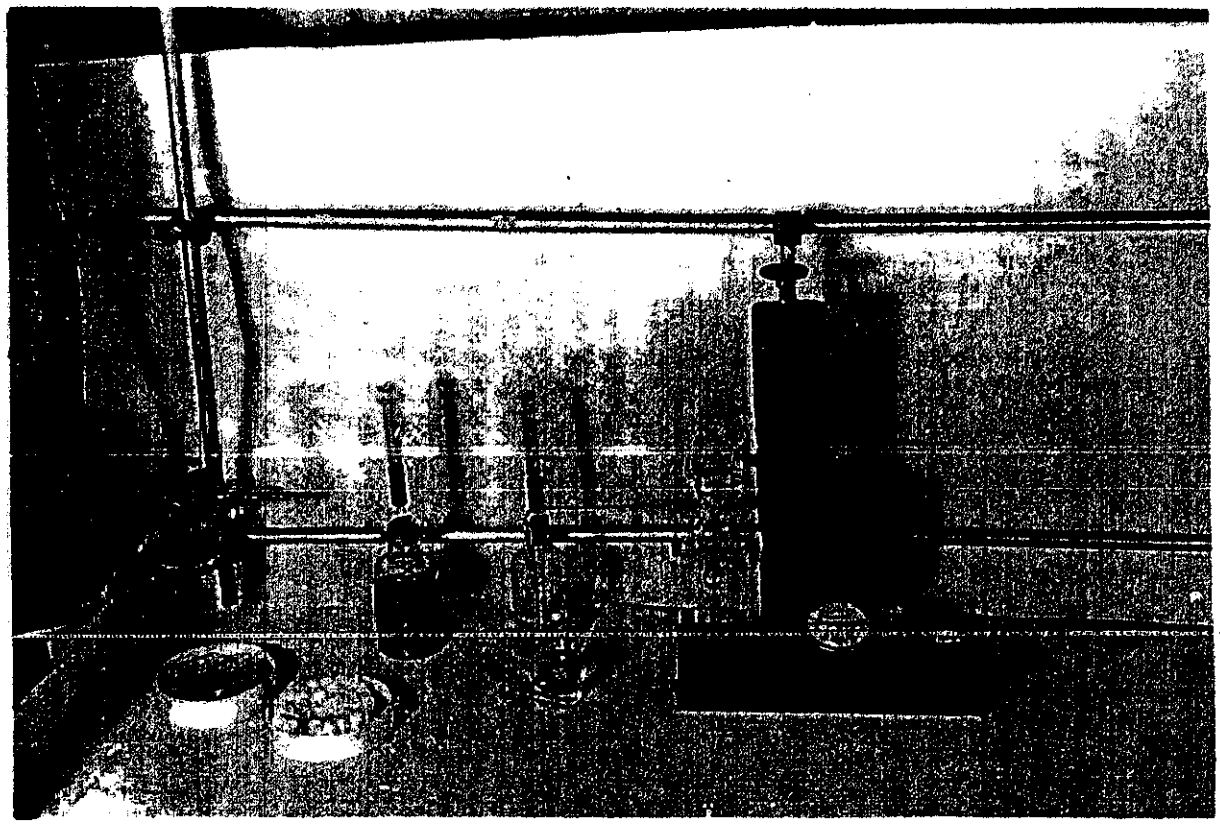

FIGURE 5

TITRATION ASSEMBLY

AEC-GE-RICHLAND, WASH.

Procedure (0.2 - 3.0 μg fluoride)

A. Sample Analysis

1. A weighed sample containing not more than 3.0 μg of fluoride is dissolved in a centrifuge cone with 1.5 ml of 3N H_2SO_4. Centrifuge the solution for two minutes and transfer the solution to a second cone if there is any undissolved residue.

2. Add 1.5 ml concentrated H_2SO_4 to the solution and stir with a platinum wire. Centrifuge for two minutes and transfer the supernate back into the original cone containing the residue.

3. Repeat step 2, using 0.5 ml of 18N H_2SO_4 rather than the concentrated. Transfer the supernatant, wash, and residue to the still and collect distillate at the rate of 1.5 ml per minute until 25 ml are collected.

4. Add 0.10 ml of 0.04 M barium acetate and 0.70 ml of indicator buffer solution (note 1). Titrate with 0.001 M thorium nitrate until the color matches that of a freshly prepared comparator solution containing the above reagents, 25 ml distilled water, and sufficient thorium nitrate to be in the region of most rapid color change (usually around 40 μl thorium).

5. The distillate from a reagent blank is titrated and the result is subtracted from the sample titration. It is sometimes necessary to make several blank distillations to clean the apparatus of residual fluoride. Blanks should not require more than 14 μl thorium solution above that used for the comparator.

B. Determination of Titration Factor

1. Follow the procedure outlined in "A" replacing the metal solution with quantities of sodium fluoride standard varying

from 0.2 to 3.0 μg F^-.

B. Determination of Titration Factor

2. Calculate by the method of "least squares" the titration factor in μg F/μl thorium.

Note 1: Makeup of indicator-buffer solution. Add 0.240 g chrome azurol-S concentrate (Geigy Co., New York City), 11.4 g monochloracetic acid and 1.4 g sodium monochloracetate in one liter of solution.

ABSTRACT

A titrimetric method for the determination of fluoride in plutonium is reported. Prior to a steam distillation of the fluoride, the bulk of the plutonium is separated by precipitation of the sulfate. The fluoride in the distillate is titrated at a pH of 3.2 with 0.001 M thorium nitrate, using chrome azurol-S indicator. Applied to samples containing 1 to 15 parts per million fluoride, the recovery is 87% and the precision on the 95% confidence level is ± 0.65 ppm.