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Report written:
February 15, 1952

LA-1369

This document consists of 29 pages

[redacted] Series A

MICRODETERMINATION OF FLUORIDE IN PLUTONIUM METAL

by

K. S. Bergstresser

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ABSTRACT

An analytical procedure for the microdetermination of fluoride in uranium metal was modified to permit its use with plutonium. Metal samples are dissolved in dilute sulfuric acid. With an increase in acid concentration about 90 percent of the resulting Pu(III) sulfate is removed from solution by precipitation. The remaining solution, containing 10 to 20 mg of plutonium and any fluoride originally in the metal sample, is transferred to an all-glass, constant-temperature still of improved design. The fluoride, separated by distillation at 135° C and collected in the distillate, is determined by titration with 0.001 M thorium nitrate and Chrome Azurol S as indicator.

Plutonium was found to be similar to uranium in that the metal formed by reduction of a plutonium salt contained more fluoride than metal which had been remelted. With plutonium samples having a uniform distribution of fluoride, a standard deviation of approximately 10 percent of the fluoride content was obtained in replicate determinations in the range of 5 to 30 ppm. For 1 to 5 ppm the standard deviation was one ppm or less. Completion of 16 individual determinations can be accomplished by one analyst in an 8-hour day.

Introduction

Recently an analytical method was developed for the determination of microgram quantities of fluoride in uranium metal.(1) This procedure has shown distinct advantages with respect to precision and time required for analysis. Therefore, it was found profitable to search for modifications which would permit its use in the microdetermination of fluoride in plutonium metal. The resulting experimental investigation and a recommended analytical procedure are described in this report. Review of the literature on analysis for fluoride is not included since this may be found in the previous report dealing with uranium metal samples. McKenna(2) has also prepared an extensive review of methods for fluoride determination.

Replacing uranium with plutonium as the material under investigation has led to changes in those sections of the experimental procedure which deal with sample dissolving and separation by distillation. In part this is due to the hazard associated with handling substances with more pronounced radioactivity. Final determination of the separated fluoride by titration with thorium nitrate and Chrome Azurol S as indicator remains essentially the same except for some improvements in construction of the microburet. Dissolving plutonium in a non-volatile acid does not require the electrolytic oxidation used for uranium samples. Fluoride separation by distillation continues to be part of the procedure, but with a still re-designed to permit its use in a well-ventilated hood and to yield more complete separations.

In the experimental work which is described and in the subsequent discussion it is understood that the plutonium metal to which reference is made is actually an alloy containing approximately 1 percent gallium unless a specific statement of some other metal composition is made.

APPARATUS AND REAGENTS

CAUTION

> Work with plutonium-containing materials should always be done in laboratories designed for adequate protection of the worker and under approved conditions. Health-Safety Rules of the Laboratory for protection from radioactive material must be strictly followed in employing any of the analytical procedures which are described in this report.

APPARATUS

The distillation procedure requires the use of an all-glass, constant-temperature still, a 230-watt Glas-Col heater (# S-400) to maintain the liquid in the outer compartment of the still at boiling temperature, a reflux condenser attached to the still to prevent loss of the boiling liquid, an electrically-heated steam generator, and a variable autotransformer for control of the steam generating rate. An arrangement of a two-still unit in a hood is shown in Figure 1. Detailed construction of the glass still (Design # B), without an attached reflux condenser, is illustrated in Figure 2. A glass still, shown to the left in Figure 3 and made according to an earlier design # A, has a different position for the sample opening and also has the condenser

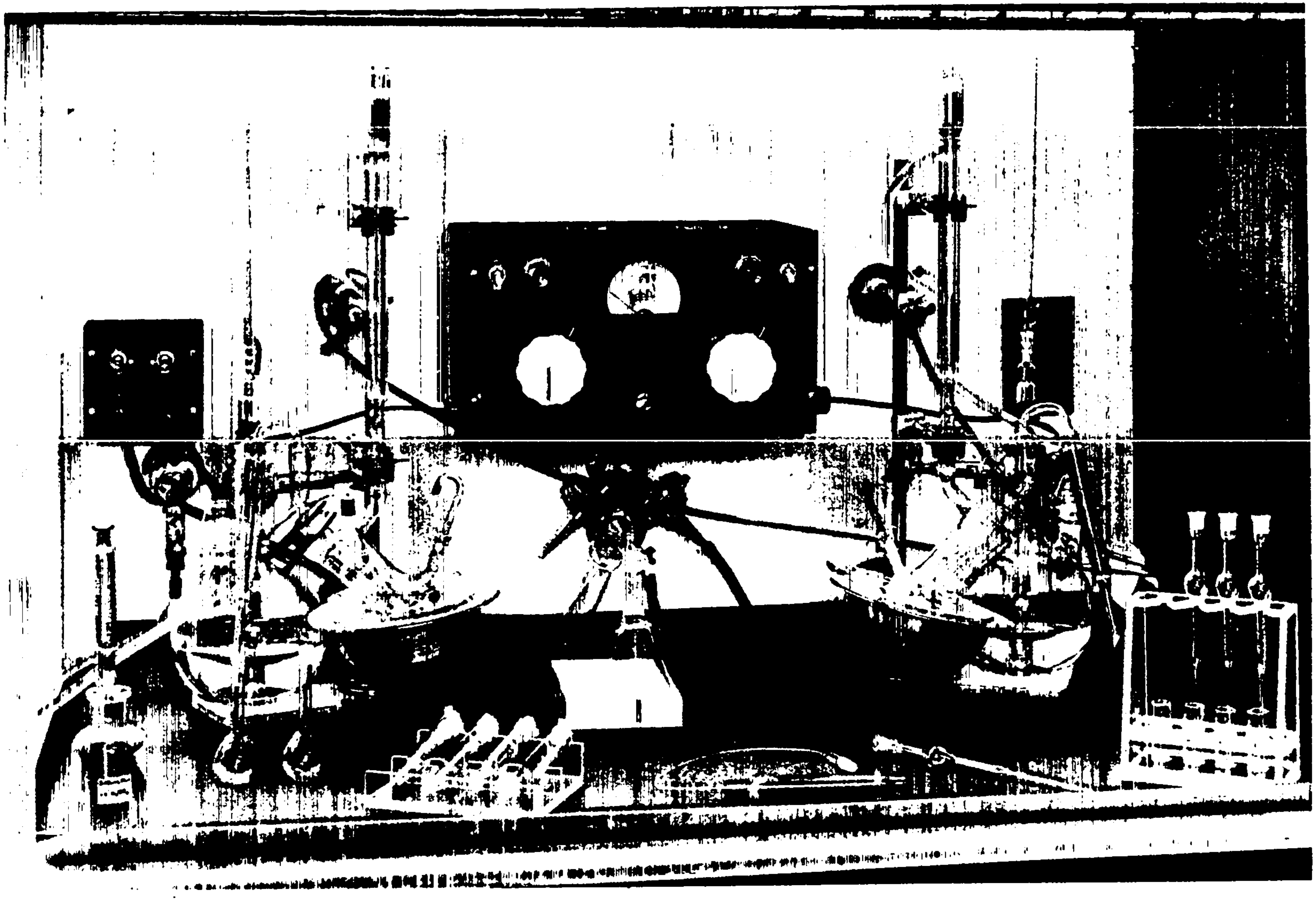
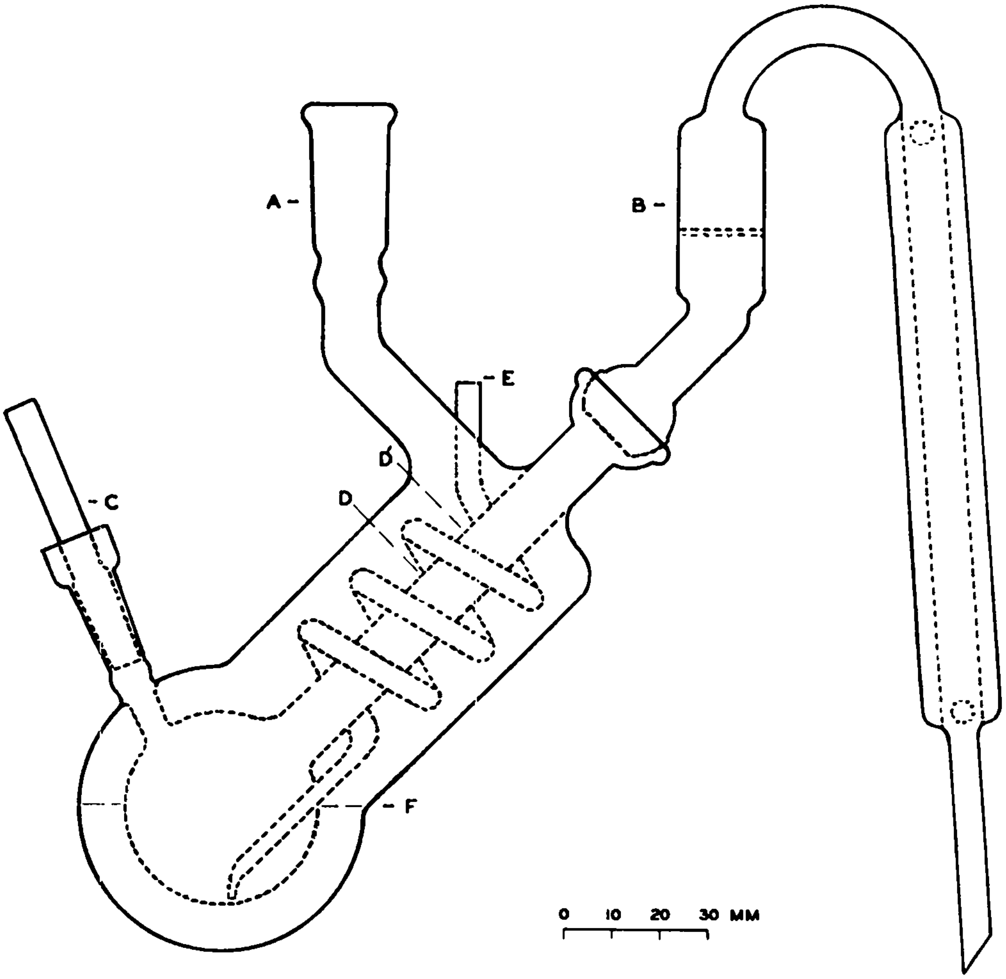


Figure 1

MICRO DISTILLATION APPARATUS

FOR FLUORIDE SEPARATION



A - 14/35 $ JOINT FOR CONNECTING REFLUX CONDENSER
B - SPRAY TRAP WITH 11MM SQUARE BAFFLE PLATE
C - OPENING TO SAMPLE COMPARTMENT, 7/25 $
D,D' - POSITION OF GLASS WOOL BAFFLE IN INNER TUBE
E - STEAM INLET
F - LEVEL OF BOILING S-TETRACHLOROETHANE

Figure 2

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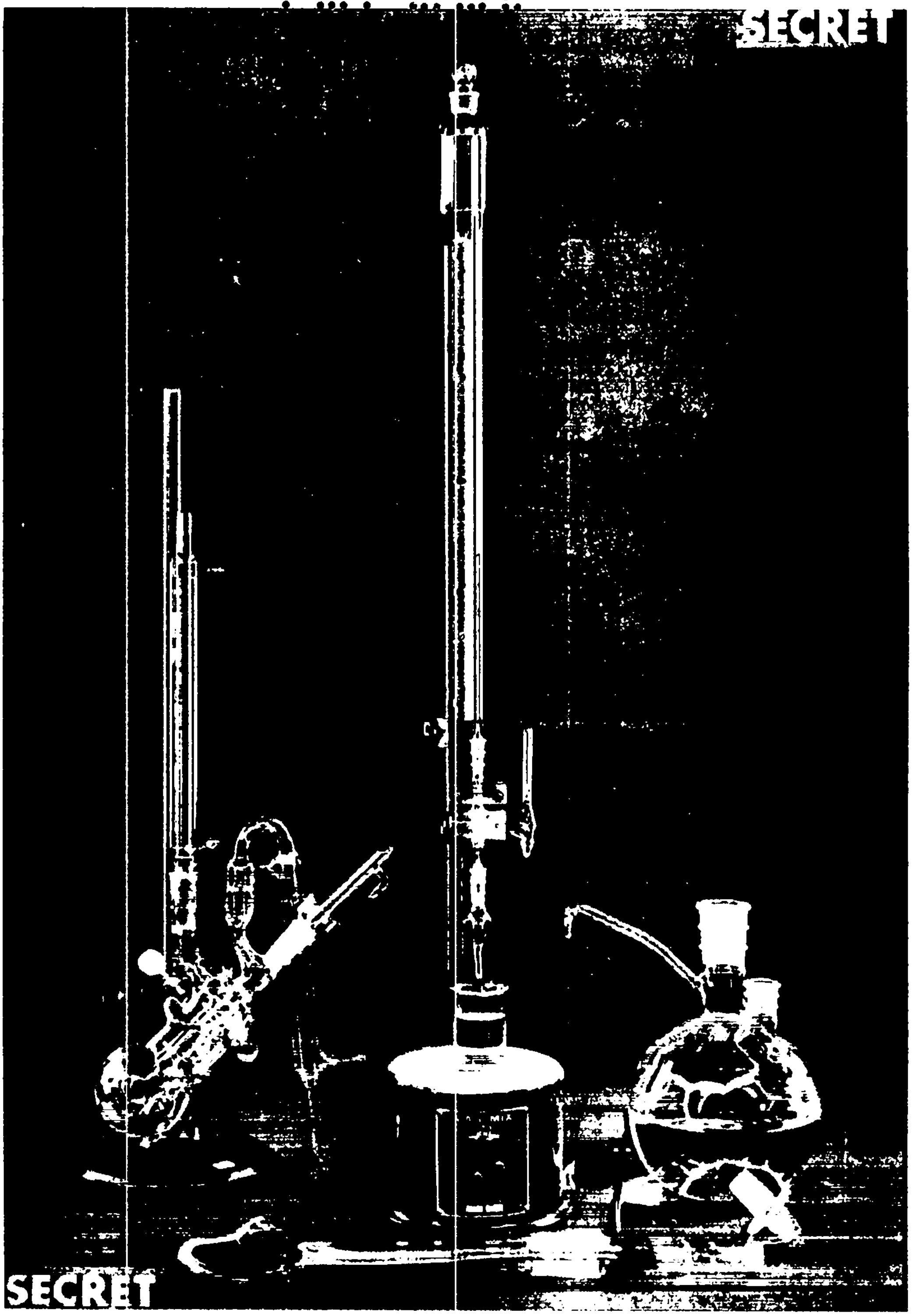

Figure 3

[redacted]

for collecting distillate permanently connected to the tube leading from the sample compartment. In this same figure there is also shown a steam generator with the heating coil and coil support removed from the flask.

The spherical sample compartment of the still with a steam exit tube at 45° to the vertical requires less space and is convenient for the necessary manipulations in a hood. The ball and socket joint connecting the steam exit tube and condenser makes it possible to readily rinse the tube and insert a section of glass wool to assist in preventing acid and plutonium salt from being carried over into the condenser and distillate. The inner compartment of the still is heated to 135-136° C by refluxing s-tetrachloroethane (at an average atmospheric pressure of 585 mm at Los Alamos). Moderate refluxing is maintained continuously during the distillation procedure by connecting the Glas-Col heater to a variable autotransformer adjusted to an output of 90 volts.

Steam is produced in a 1-liter flask in which is supported a 55-ohm resistance coil, prepared by winding a 21-foot length of # 26 B and S nichrome wire over a 5/16-inch diameter mandrel. The coil support also has an inner 5-mm tube which, when extended to a height of 75 cm by another section of 5-mm tubing, serves as a safety tube in case excessive pressure should be produced in the flask. The coil support was made from a reduced tube 29/42 ₮ inner joint and platinum wires were used in making electrical connection through the glass. Another practical arrangement for a steam generator has been described recently.(3)

In using the steam generator it is quite essential to remove the stopper from the one-liter flask before reducing the potential supplied to the heating coil by the variable autotransformer; otherwise, the acid-plutonium solution will be drawn back into the generator.

A 300 microliter-capacity microburet was constructed from a 35 cm length of 1.13 mm-I.D., precision-bore capillary tubing, mounted rigidly before a metric scale on a length of 3/8 x 1-1/2-inch dural as shown in Figure 3. In this manner the millimeter divisions on the scale correspond to microliters for the buret. The handle of the stopcock was extended to give more accurate control when 1 or 2 microliter increments of the titrating solutions were being added. A plastic rack for holding 15 ml centrifuge cones at a slight angle above horizontal, during the dissolving of plutonium metal samples, is shown in the foreground in Figure 1. At the extreme right in the same figure there is another plastic rack prepared to support transfer pipets and 16 x 50 mm test tubes. Plutonium solutions are transferred to these test tubes after centrifuging and before transfer to the still.

REAGENTS

Sodium Fluoride: Reagent-grade sodium fluoride was recrystallized once and dried at 500° C for 8 hours. To prepare a solution containing 5 micrograms of fluoride per ml, 0.2210 gm of this recrystallized material was dissolved in water and diluted to one liter. A 50 ml aliquot of this first solution was diluted to 1 liter to obtain the final solution which was stored in a 1-liter alkali-resistant bottle (Corning Glass No. 728). Other standard fluoride solutions were prepared and stored in a similar manner.

Thorium Nitrate: A 0.001 M solution was prepared by dissolving 0.552 gm of reagent-grade $Th(NO_3)_4 \cdot 4\ H_2O$ in water and diluting to 1 liter.

Buffer-Indicator Solution: A 0.04 percent solution of the indicator in 0.24 M half-neutralized chloroacetic acid was prepared by dissolving 40 mg of Chrome Azurol S, Concentrate (Geigy Company, Inc., New York) in 100 ml of the buffer. After allowing this solution of the indicator to stand overnight, it was filtered through a retentive filter paper before use. The 0.24 M buffer solution was prepared by dissolving 11.35 gm of chloroacetic acid (Eastman No. 68) in water and diluting to 100 ml. A 50 ml portion of this acid solution was removed and neutralized to a phenolphthalein endpoint with 6 N KOH. The acid and neutralized solutions were quantitatively transferred to a 500 ml volumetric flask and diluted to volume. The buffer-indicator solution prepared in this manner is stable indefinitely.

Barium Acetate: A 0.04 M solution was obtained by dissolving 1.1 gm of reagent-grade $Ba(C_2H_3O_2)_2 \cdot H_2O$ in 100 ml of water.

Sulfuric Acid: 5 N H_2SO_4, 70 ml of concentrated acid diluted to 500 ml. 3:1 H_2SO_4, 3 volumes of concentrated acid and one volume of water are mixed. 1:1 H_2SO_4, equal volumes of concentrated acid and water are mixed.

All water used was double distilled.

RECOMMENDED PROCEDURE

(1) Weigh a 0.200 gm sample of plutonium metal, with a fluoride content not greater than 10 micrograms. If the metal contains more than 50 ppm of fluoride, a smaller sample should be used.

(2) Transfer the sample to a 15 ml centrifuge tube.

(3) Add 1.0 ml of 5 N H_2SO_4 to the metal, immediately close the tube with a stopper made from a piece of Kleenex tissue, and support the tube at an angle slightly above horizontal, to direct most of the spray against the inner glass surface of the tube.

(4) When the metal has dissolved completely, usually within 30 minutes, remove and discard the Kleenex tissue and add with stirring 2 ml of 3:1 H_2SO_4 to the blue plutonium sulfate solution. A heavy platinum wire can be used for stirring and agitation should continue until a uniform mixture is certain.

(5) Allow the precipitated plutonium sulfate crystals to settle for 15 to 20 minutes and then centrifuge the tube and contents for one minute.

(6) Transfer the supernatant liquid from the tube with a syringe-pipet to a 16 x 50 mm test tube. Support the pipet with its tip resting in the test tube, until further use is required.

(7) Add 0.5 ml of 1:1 H_2SO_4 to the plutonium sulfate crystals in the centrifuge tube and agitate the mixture thoroughly with a platinum stirring rod.

(8) Centrifuge the tube and contents for a short time.

(9) Transfer the supernatant liquid, with the same syringe-pipet used in step (6), from the centrifuge tube to the test tube containing the main portion of acid solution. Again support the pipet with its tip resting in the test tube until the combined solution is to be transferred to the distillation apparatus.

(10) Dissolve the plutonium sulfate crystals in the centrifuge tube in dilute sulfuric acid and transfer the solution by suction to a bottle for recovery solutions.

(11) Prepare the distillation apparatus for use by connecting the Glas-Col heater to a 90-volt outlet and heating the water in the steam generator to boiling by increasing the output of the controlling autotransformer to a maximum (135 volts). The stopper to the steam flask should be removed.

(12) When the water is heated to boiling, reduce the steam generating rate, so that 25 ml of distillate will be collected in 15 to 20 minutes, by changing the autotransformer output to about 75 volts. Replace the stoppers to the steam flask and the sample compartment opening and collect 50 to 75 ml of distillate before beginning a series of distillations. This distillate is slightly radioactive and should be transferred to an appropriate container.

(13) Remove the stopper from the steam flask and then the stopper from the sample-compartment opening.

(14) Using the same syringe-pipet employed in steps (6) and (9), transfer, without rinsing, the entire solution sample to the sample compartment.

(15) Immediately replace the stoppers to the sample compartment and the steam flask.

(16) Place a 25 ml volumetric flask in position to collect the first 25 ml of distillate.

(17) When the flask is just filled to the mark, replace it with another 25 ml volumetric flask to collect the second 25 ml aliquot of distillate.

(18) When this second flask is filled to the mark replace it with a 125 ml Erlenmeyer flask.

(19) Remove the stopper from the steam flask and then the stopper from the sample-compartment opening.

(20) Remove the sample solution from the inner compartment of the still with an all-glass suction tube and flask. With the suction tube remaining in the compartment opening, add distilled water from a wash bottle to thoroughly rinse out all sample solution.

(21) After removing all liquid from the sample compartment by suction, another sample may be added and the procedure repeated beginning with step (14).

(22) Transfer the 25 ml aliquots of distillate to separate 30 ml beakers

which also contain glass-enclosed magnetic stirrers.

(23) Prepare, if necessary, a solution for color comparison at the end-point of the fluoride titration by mixing thoroughly the following in a 30 ml beaker: 25 ml of distilled water, 0.50 ml of buffer-indicator solution, 0.20 ml of 0.04 M barium acetate, and 100 microliters of 0.001 M thorium nitrate, the last solution from the microburet to be used in the subsequent titrations.

(24) Add the same volume of buffer-indicator and barium acetate solutions to the 25 ml aliquot of distillate which was collected in the second 25 ml volumetric flask.

(25) Add 0.001 M thorium nitrate solution from the microburet, using continuous, rapid stirring, until the color is identical with that of the color comparison solution. An exact matching of the color is not essential and the bluish-pink color of a freshly-prepared comparison solution may be judged from memory.

(26) Record the volume of 0.001 M thorium nitrate added to this second 25 ml aliquot of distillate.

(27) Add the same volume of buffer-indicator and barium nitrate solutions used in steps (23) and (24) to the 25 ml aliquot of distillate which was collected in the first 25 ml volumetric flask.

(28) Add 0.001 M thorium nitrate solution from the microburet, using continuous, rapid stirring, until the color exactly matches that of the second 25 ml of distillate which was titrated in step (25). This comparison should be made as soon as possible after completing step (25).

(29) Record the volume of 0.001 M thorium nitrate solution added to this first 25 ml aliquot of distillate.

(30) Subtract the volume recorded in step (26) from the volume recorded in step (29) to obtain the thorium nitrate equivalent to the fluoride content of the analysis sample.

(31) Standardize the thorium nitrate solution used in titration by beginning with step (14), but replacing the acid solution of plutonium sulfate with 4 or 5 ml of 1:1 H_2SO_4 to which has been added a known amount of fluoride (as NaF) in the form of an aqueous solution with a volume not greatly exceeding 0.5 ml.

DISSOLVING METAL SAMPLES

If trace amounts of fluoride are to be separated by distillation, the sample containing fluoride must be added to the still as a solution of some non-volatile acid. At first 60 percent perchloric acid was used for this purpose because plutonium is more soluble in this reagent than in sulfuric acid, at the acid concentration required by the distillation procedure. Perchloric acid is partially reduced to chloride in dissolving 100 mg plutonium samples; therefore it was necessary to add silver perchlorate to the sample solution to avoid collecting hydrochloric acid in the distillate.

In the analysis of plutonium samples dissolved in perchloric acid, to which known microgram amounts of fluoride were added, only about 50 percent of the added fluoride could be recovered in 25 ml of distillate if the sample was the 1 percent gallium alloy. With plutonium metal containing no more than trace amounts of other elements, almost complete recovery of the added fluoride was observed. If an aliquot of this dissolved high-purity plutonium was first modified by adding to it gallium sulfate in an amount equivalent to a 1 percent alloy, then this solution also gave low fluoride recoveries. Acting on the assumption that a complex ion, such as GaF_6^{-3}, might lose its fluoride content slowly at 135° C in perchloric acid solution and in the presence of a relatively large quantity of trivalent plutonium, a sample of the dissolved plutonium-gallium alloy was first oxidized to Pu(IV) before distillation. Sodium dichromate or chromium trioxide in perchloric acid was used for oxidation. Under these conditions the presence of gallium did not interfere with the distillation and the added fluoride was recovered satisfactorily. However, when Cr(VI) was employed in oxidizing plutonium, an excess of oxidizing agent had to be avoided. Otherwise chromyl chloride was formed and carried over into the distillate at times to give it a noticeable color and always to interfere with the titration.

Another observation made while using perchloric acid for dissolving metal samples, involved the formation of a non-uniform draining surface inside the condenser of a still similar to the one shown in Figure 3. After collecting distillate from about 15 successive samples, the tube from the spray trap to the condenser and the inner surface of the latter had the appearance of being dirty and condensate collected in droplets instead of forming a uniform liquid film on the glass. This condition could be removed by adding a mixture of sulfuric and concentrated nitric acids to the still and continuing distillation for 5 or 10 minutes. It would appear again after collecting distillate from a series of perchloric acid samples although every effort was made to remove any possible organic material from the samples and equipment before distillation.

It was necessary to avoid this non-uniform draining surface in the still to be certain that all condensate carrying fluoride would drain into the volumetric flask collecting the first 25 ml of distillate and prevent liquid containing fluoride from collecting in the second 25 ml of distillate where it would be titrated as part of the analysis blank. Actually it was found that all analyses made, when the condensate would not drain properly, had low results. It was concluded that the non-uniform surface was produced by formation of some insoluble plutonium compound, deposited on the glass because of hydrolysis in regions where the acidity was decreased sufficiently. This explanation seemed plausible after noticing that the non-uniform draining of condensate occurred after distillation of several samples, if the sample weight was increased from 100 mg to 300 mg or if a still was used in which the 11 mm-square baffle plate was omitted from the spray trap.

Because it was possible to only partially overcome some of the difficulties associated with the use of perchloric acid in dissolving plutonium samples, a change was made to sulfuric acid although Behling, Christopherson, and Kendall(4) report that plutonium is not soluble in sulfuric acid. Actually the lower solubility in this reagent was taken as an advantage and used in making a preliminary separation by precipitation of 90 percent of the plutonium sulfate before subjecting the solution containing fluoride to distillation. It was found that 200 mg of plutonium-gallium alloy will completely dissolve in 0.5 to 1.0 ml of 5 N H_2SO_4 in 30 minutes or less. The resulting Pu(III) sulfate solution is not stable and must not be allowed to stand indefinitely. Heating the sample during dissolving will cause the formation of plutonium sulfate crystals, preventing complete dissolution of the metal. If 200 mg of plutonium is dissolved in much less than 0.5 ml of 5 N H_2SO_4, reaction time is increased, air oxidation occurs, and precipitation of the less soluble Pu(IV) sulfate may make impossible the complete dissolving of the sample. This same condition may result with high-purity plutonium and 1.0 ml of 5 N H_2SO_4 since the pure metal requires a longer reaction time. If no condition is permitted which will disturb the apparently supersaturated solution of Pu(III) sulfate, it is possible to bring the entire sample into solution. Then the acid concentration may be increased to precipitate most of the dissolved metal and retain the trace amount of fluoride in the supernatant liquid along with a fraction of the plutonium sulfate.

ANALYTICAL RESULTS AND DISCUSSION

After developing a method for dissolving plutonium with sulfuric instead of perchloric acid, investigation was directed toward estimating the accuracy which might be reasonably expected in determining the fluoride present in 100 to 200 mg metal samples, in the range of one to 30 ppm. For this purpose 500 to 600 mg samples of plutonium-gallium alloy were dissolved in 2 to 3 ml of 5 N H_2SO_4. Each of these solutions was divided into four aliquots and to the latter were added varying known amounts of fluoride in volumes no greater than 0.5 ml. One aliquot in each group of four had 0.2 ml of distilled water added in place of fluoride solution, to serve as a blank and permit determination of any fluoride in the original plutonium metal. The additions of fluoride to the aliquots, as a NaF solution of known concentration, were made by individuals other than the analyst and the amounts were not known to him until after he had completed the analyses.

In making these fluoride determinations the essential details of the recommended procedure were followed, using a glass still without a glass wool baffle and similar to the one illustrated in Figure 3 (Design # A). The data secured in this manner are given in Table I.

Table I

Determination of Fluoride Added to Plutonium Solutions

Pu Sample No.	Fluoride Added (Micrograms)	Fluoride Found (Micrograms)	Error (Micrograms)
A	0.5	0.3	- 0.2
	2.5	2.1	- 0.4
	0.0	0.0	0.0
	1.0	0.7	- 0.3
B	1.5	1.3	- 0.2
	2.0	2.1	+ 0.1
	0.0	0.1	+ 0.1
	0.0	0.1	+ 0.1
C	2.0	1.8	- 0.2
	0.5	0.5	0.0
	0.0	0.0	0.0
	0.5	0.4	- 0.1
D	2.0	1.9	- 0.1
	1.0	1.0	0.0
	0.0	0.0	0.0
	1.5	1.1	- 0.4
E	1.2	1.2	0.0
	3.0	2.9	- 0.1
	0.0	0.0	0.0
	0.6	0.4	- 0.2
F	0.0	0.0	0.0
	0.9	1.0	+ 0.1
	2.4	2.1	- 0.3
	1.8	1.8	0.0

In this group of analyses the weight of fluoride, added to each solution containing 125 to 150 mg of dissolved plutonium, varied between 0.0 and 3.0 micrograms. The fluoride was determined with a maximum error of 0.4 micrograms and a mean error of ± 0.12 micrograms for the 24 determinations. The over-all accuracy for the 17 aliquots to which fluoride was added is indicated by the mean error of ± 13 percent.

In addition to the reported results, the thorium nitrate solution used in titration was standardized by adding 1.0 microgram amounts of fluoride to 3.5 ml of 1:1 H_2SO_4. These mixtures were transferred to the glass still; distillates were collected and titrated in the usual manner. For seven determinations the mean volume of thorium nitrate was 29 microliters with a standard deviation of 1.3 microliters, equivalent to 1.0 ± 0.04 micrograms of fluoride. Consequently the standardization was appreciably more precise than the determinations for fluoride added to plutonium solutions. It was concluded tentatively that with 100 to 200 mg plutonium samples, average errors of 1 to 3 ppm could be expected when the range of fluoride content was 2 to 30 ppm.

Before continuing with additional determinations, possible improvements in the design of the distillation equipment were considered. This was a result, in part, of the observation made from the preceding experiments where the standardization data, involving no separation from plutonium, were more precise than the data obtained with a procedure which did include a plutonium separation. Also, it had been found that plutonium and sulfate do interfere to some extent with the thorium nitrate titration. For example, when 19 micrograms of plutonium was added to 25 ml of distilled water containing 5.4 micrograms of fluoride, titration with $Th(NO_3)_4$ indicated that only 4.0 micrograms of fluoride were present.

Observations were made concerning the quantity of plutonium collected under various conditions in 25 ml of distillate. For this purpose plutonium was estimated with radiochemical determinations. It was found that 25 ml of distillate contained from 0.1 to 72 micrograms of plutonium, the latter when a 300 mg metal sample was present in the still. When the recommended procedure is employed, about 90 percent of the 100 to 200 mg sample is separated by precipitation and only 10 to 20 mg of plutonium is actually added to the still. Under these conditions the amount of plutonium collected in 25 ml of distillate frequently varied between 0.2 and 0.9 microgram.

When a change was made to the still designed to include a glass wool baffle (Figure 2), a decrease in both plutonium and sulfuric acid collected in the distillate was noted. For 25 ml volumes the plutonium varied between 0.01 and 0.001 microgram and the pH of the distillate was 4.9 to 5.2 instead of the former range of 3.0 to 4.0. To determine the effectiveness of this glass-still modification, in terms of fluoride separation and titration only, a temporary change in procedure was made. Precipitation of Pu(III) sulfate was eliminated and analysis began with a sulfuric acid solution containing 10 to 15 mg of plutonium. To this sample solution was added a known amount of fluoride, or distilled water, and sufficient concentrated acid to obtain 4 ml of final mixture containing approximately 50 percent sulfuric acid by volume. The results for samples containing 0, 1, and 5 micrograms of fluoride are presented in Table II.

Table II

Titration Reproducibility for Fluoride Separated From Plutonium with Still Containing a Glass Wool Baffle

	Volume of 0.001 M $Th(NO_3)_4$, Microliters		
Fluoride Added to Each Sample, Micrograms	0*	1	5
	-1	27	122
	0	29	136
	-2	30	120
	-1	30	130
	1	28	132
	-1	29	135
		29	129
		27	137
Mean volume per microgram of fluoride		28.6	26.3
Standard Deviation		1.1	1.2

* Negative volumes result when the titration blank, obtained in titrating the second 25 ml of distillate, is slightly greater than the volume of $Th(NO_3)_4$ used in titrating the first 25 ml of distillate.

The data in Table II reveal that good reproducibility can be expected in using the new glass still for separation of fluoride from plutonium and that the precision is just as satisfactory as that obtained with the earlier design of still when it was used for separating fluoride from solutions containing only sulfuric acid and no plutonium. Reproducibility is approximately equal for samples to which 1 or 5 micrograms of fluoride were added. The difference in average volume of thorium nitrate per microgram of fluoride for 1 and 5 micrograms is statistically significant and indicates that a non-linear relationship exists between the amount of fluoride in a sample and the volume of $Th(NO_3)_4$. This observation also has been reported by Milton, Liddell, and Chivers.(5)

Plutonium samples available for the analytical investigation reported in Table I were representative of the metal turnings which resulted when several smaller portions of metal were re-melted, cast into various shapes, and machined. This re-melted metal contained no more than 1 ppm of fluoride, according to results in Table I, for the seven samples which were not treated with added fluoride. Moreover, similar results were obtained with another group of samples from re-melted metal; the maximum fluoride content for the twenty samples was 2 ppm. In order to make fluoride determinations on metal samples with results appreciably above 2 ppm, and without adding sodium fluoride to the dissolved plutonium, it was necessary to secure metal directly after it was produced by reduction of a plutonium compound and before it had been re-melted. Analytical data for metal which has not undergone re-melting are reported in Table III.

Table III

Determination of Fluoride in Plutonium Metal Before Re-Melting

Metal Sample	J	K	L	M	Q
Fluoride, ppm	1.8	7.3	1.5	0.7	12.4
	1.2	10.6	1.1	0.9	24.6
	1.6	7.4	2.1	0.9	11.7
	0.2	8.5	2.2	5.1	16.7
Average, ppm	1.2	8.5	1.7	1.9	16.4
Standard Deviation	0.7	1.5	0.5	2.1	5.9

It may be observed in Table III that the average fluoride content of plutonium varies between 1 and 16 ppm and that some of the samples show a decided lack of precision. Since similar observations were made when analyzing uranium metal which had not been re-melted,(6) it was assumed that the high values for standard deviation recorded in Table III were partly reflecting the fact that the plutonium metal was non-homogeneous with respect to fluoride. To verify this assumption additional fluoride determinations were made, but with the following change in analytical method. After four 200 mg portions of plutonium for each metal sample were dissolved in accordance with step (3) of the procedure, the four solutions were combined, mixed thoroughly, and then divided into four volume aliquots before continuing with the procedure as described in step (4). In this manner influence on measurement of analytical precision by the non-homogeneous character of the metal was eliminated. Results for such determinations are given in Table IV. In all cases there is a decided increase in precision, making it reasonable to conclude that plutonium metal which has not undergone a re-melting process is not homogeneous in its fluoride content.

Table IV

Determination of Fluoride in Aliquots Taken From Combined Solution of Four Metal Samples

Metal Sample	J	K	N	O	P
Fluoride, ppm	11.9	8.2	5.5	10.2	1.1
	11.4	7.7	5.2	11.9	1.5
	9.9	7.1	5.5	10.2	1.5
	11.9		5.5	10.8	1.2
Average, ppm	11.3	7.7	5.4	10.8	1.3
Standard Deviation	1.0	0.6	0.2	0.8	0.2

Analytical data in Tables III and IV illustrate the precision which may be expected in determining fluoride in plutonium metal. To obtain some indication of the accuracy, two determinations were made with solution aliquots which were identical with, and prepared at the same time as, the aliquots used to secure the results listed in Table IV under metal sample J. However, before continuing the analyses with procedure step (4), these two aliquots had their fluoride content increased by 1.0 microgram through addition of sodium fluoride. After subtracting 1.0 microgram from the amounts of fluoride which were determined by completion of the analyses, 2.2 and 2.3 micrograms, the fluoride content of the metal was calculated as 10.9 and 11.4 ppm. These results are in good agreement with the average value of 11.3 ppm for the four aliquots to which no sodium fluoride was added.

CONCLUSIONS

An analytical procedure is proposed for the determination of fluoride in plutonium metal. With samples having a uniform distribution of fluoride, a standard deviation of approximately 10 percent of the fluoride content may be expected in the range of 5 to 30 ppm for replicate determinations and for 1 to 5 ppm the standard deviation is one ppm or less. It is reasonable to expect completion of 16 individual determinations by one analyst in an 8-hour day.

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