[redacted] DECLASSIFIED

HW-20036

Chemistry - General

This document consists
of 13 pages [redacted]
(page 8 Unclassified)

BEST AVAILABLE COPY

ANALYTICAL PROCEDURES FOR THE PLUTONIUM METAL FABRICATION PROCESS
XI. THE DETERMINATION OF FLUORIDE

Experimental Work
by
G. J. Behling and E. W. Christopherson

Written
by
L. F. Kendall
Analytical Section
Technical Services Division

January 15, 1951

Classification Cancelled (Change to
DECLASSIFIED
By Authority of H. F. Carroll,
DBORE, 3-8-60
By W. Ramus 4-4-60
RL Orgill 2/12/99

HANFORD WORKS
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission
by the
General Electric Company
under
Contract # W-31-109-eng-52

Route To	Read By	Date	Route To	Read By	Date
[illegible]	aBY/oy				
[illegible]					
[illegible]	[illegible]	[illegible]			

THIS DOCUMENT IS PUBLICLY AVAILABLE

[redacted]

DECLASSIFIED

DECLASSIFIED

[redacted]

COPY NUMBER	INTERNAL DISTRIBUTION
1	A. B. Greninger - O. H. Greager
2	O. F. Hill
3	B. Weidenbaum - P. E. Collins
4	T. W. Hauff
5	F. W. Albaugh
6	A. H. Bushey
7	L. M. Knights - O. P. Amacker
8	W. W. Marshall - H. R. Schmidt
9	H. W. Murray
10	D. F. Shepard
11	G. J. Behling
12	E. W. Christopherson
13	G. W. Watt, University of Texas
14	L. F. Kendall
15	300 File
16	700 File
17	Pink Copy
18	Yellow Copy

[redacted]

DECLASSIFIED

DECLASSIFIED

[redacted]

COPY NUMBER	EXTERNAL DISTRIBUTION
19 - 26	Argonne National Laboratory
27	Armed Forces Special Weapons Project
28 - 32	Atomic Energy Commission, Washington
33	Battelle Memorial Institute
34 - 37	Brookhaven National Laboratory
38 - 41	Carbide and Carbon Chemicals Division (K-25 Plant)
42 - 45	Carbide and Carbon Chemicals Division (Y-12 Area)
46	Chicago Patent Group
47	Chief of Naval Research
48	Dow Chemical Company
49 - 53	du Pont Company
54	Hanford Operations Office
55 - 58	Idaho Operations Office
59	Iowa State College
60	Kellex Corporation
61 - 64	Knolls Atomic Power Laboratory
65 - 67	Los Alamos
68	Los Alamos Attn: C. F. Metz
69	Mallinckrodt Chemical Works
70	Massachusetts Institute of Technology (Gaudin)
71	Massachusetts Institute of Technology (Kaufmann)
72 - 74	Mound Laboratory
75	National Advisory Committee for Aeronautics
76	National Bureau of Standards
77	Naval Medical Research Institute
78	Naval Radiological Defense Laboratory
79	Naval Research Laboratory
80 - 82	NEPA Project
83	New Brunswick Laboratory
84 - 85	New York Operations Office
86	North American Aviation, Inc.
87 - 94	Oak Ridge National Laboratory, X-10 Site
95	Patent Branch, Washington
96	Savannah River Operations Office
97	Sylvania Electric Products, Inc.
98 - 112	Technical Information Service, Oak Ridge
113	UCLA Medical Research Laboratory (Warren)
114	U. S. Geological Survey
115 - 118	University of California Radiation Laboratory
119 - 120	University of Rochester
121	Western Reserve University (Friedell)
122 - 123	Westinghouse Electric Corporation

[redacted]

DECLASSIFIED

ANALYTICAL PROCEDURES FOR THE PLUTONIUM METAL FABRICATION PROCESS

XI. THE DETERMINATION OF FLUORIDE

INTRODUCTION

Among the determinations requested for the 234-5 Project analytical program was that of fluoride in plutonium metal samples, with a sensitivity of 0.5 p.p.m. and an accuracy of ± 100% (1).

Several fluorimetric and volumetric methods for the microdetermination of fluoride have been reported in the classified literature (2, 3). The method selected for investigation, however, was one developed for the determination of ionizable fluorine in gases in the range of 1-500 p.p.m.; this method appeared attractive because the determination depends on the generation of a color rather than on the bleaching effect or on a change of color (4).

SUMMARY

A method has been developed for the determination of 0.25-2.5 micrograms of fluoride in plutonium. After dissolving the sample in perchloric acid and separating fluoride ion by distillation of fluosilicic acid, the quantity of fluoride is determined by measuring the intensity of color generated by the reaction between the fluoride and the zirconium salt of p-dimethylaminoazophenylarsonic acid.

EXPERIMENTAL WORK

In the method described for the analysis of gases (4), a sample is drawn through a tube containing a moist mixture of sand and the zirconium salt of p-dimethylaminoazophenylarsonic acid; the colored free acid is then separated from the tube contents by elution with an acetone-hydrochloric acid mixture and transferred to a piece of filter paper. The color intensity, and thus the fluoride content of the gas, is evaluated by visual comparison with standards. The method depends upon two facts: (1) in an acidic medium the zirconium salt reacts with fluoride ion to generate the free acid and (2) p-dimethylaminoazophenylarsonic acid dissolves in a mixture of acetone and hydrochloric acid to form a deep red solution, while the zirconium salt of this acid is insoluble.

Preliminary tests indicated that the following was a feasible method for the present problem: distill fluoride from the sample as fluosilicic acid using the

Willard-Winter procedure; collect the distillate in a receiver containing the reagent; evaporate to reduce volume; extract the acid from the residue with hydrochloric acid-acetone; and measure the optical density of the filtrate. The zirconium p-dimethylaminoazophenylarsonate is prepared by adding an aqueous solution of zirconyl chloride to the acid in a mixture of ethanol and hydrochloric acid. After prolonged digestion at 60°C., the precipitate is separated by filtration, washed, and dried (4). It was found in subsequent preparations that the digestion period could be reduced substantially with a corresponding saving of time, and that modifications in the washing and drying procedures produced a better reagent.

The first investigations were made of conditions for optimum color development. After locating the absorption peak of p-dimethylaminoazophenylarsonic acid at 500 mμ, tests were performed by adding various quantities of solution containing known amounts of sodium fluoride to a mixture of 1% reagent and sea sand in 2 N hydrochloric acid in a fused silica dish. After the contents of the dish were evaporated to dryness, the residue was washed with several portions of 1:4 solution of 2 N hydrochloric acid and acetone. The liquid was decanted into a small sintered glass filter funnel, and the filtrate was collected in a five ml. volumetric flask. After dilution to volume, the optical density was read on a Beckman spectrophotometer using one cm. cells. Inconsistent and nonreproducible results were traced in part to variations in the reagent and to heterogeneity of the sand-reagent mixture. Modifications in the preparations of reagent and the replacement of the sand mixture by a water suspension of the reagent resulted in markedly improved results. Tests with a new reagent revealed that the optical density difference between blank and sample was dependent upon acidity and time during the color development. Optimum differentiation was found at 3.6 N hydrochloric acid and 30 minutes standing, higher acidities resulting in limited ranges for the determination.

Additional tests were made to determine the effect of elevated temperatures on the color development. After adding sodium hydroxide solution to give pH=9 to prevent possible loss of hydrofluoric acid, heating for 30 minutes at temperatures between 25-95°C. increased the optical density of both the sample and the blank with only slight improvement in the difference between them. The procedure decided upon for the color development was as follows:

1. Pipet a solution containing fluoride into a 50 ml. silica dish, and add 200 µl. of 0.1% suspension of reagent in water.
2. Add water, if necessary, to give a volume of 700 µl.
3. Add 300 µl. of 12 <u>N</u> hydrochloric acid, and mix immediately by swirling, then let stand 30 minutes.
4. Pour the contents of the dish into a 3 ml. fine sintered-glass filter funnel, collecting the filtrate in a 5 ml. volumetric flask.
5. Extract the free acid by washing the dish with five 500 µl. portions of acidified acetone and filtering each portion through the funnel.
6. Dilute the filtrate to 5 ml. with acidified acetone and mix. Measure the optical density at 500 mµ, using a one cm. cell.

It was found that this procedure provided determinations in the range 0.25-2.5 µg. of fluoride with a difference of 3-5% between samples.

The above procedure was coupled to the distillation step by making the distillate alkaline with sodium hydroxide, evaporating to dryness, and dissolving the residue in 500 µl. of water. The Willard-Winter procedure consists of dissolving the sample to form hydrofluoric acid and steam-distilling fluosilicic acid, formed by the reaction of the hydrofluoric acid on the glass vessel, from sulfuric or perchloric acid at about 140°C.; since plutonium is not soluble in sulfuric acid, it was necessary to use perchloric acid for this problem. Determinations of known quantities of fluoride added to the distilling flask were erratic and several designs of the still were tried before satisfactory results were obtained; the final design is shown in Figure 1.

The use of perchloric acid presented a problem, since it was realized that with the sensitivity limit for the method at 0.25 µg., a 0.5 g. sample of plutonium would be required to determine 0.5 p.p.m. This made imperative the use of a gloved box for this operation, which then entailed the use of hot perchloric acid in a wooden box equipped with rubber gloves. Efforts were therefore made to lessen the hazards of the operation. Mixtures of sulfuric and perchloric acids do not dissolve even small samples, while the addition of sulfuric acid to the sample dissolved in perchloric acid results in considerable frothing and bumping during the distillation. It was decided therefore to use 1 10 perchloric acid for the dissolving and 57% perchloric acid for the distillation. A steel shield was built around the distilling flask to prevent spattering and to hold the acid in case of breakage.

[redacted]

The precision for several results obtained with standard sodium fluoride solutions using the procedure as finally written is shown in Table I.

TABLE I
PRECISION OF DETERMINATIONS OF FLUORIDE IN STANDARD SOLUTIONS

μg. F^-	No. of Determinations	Average O. D.	Precision (O. D.) 99% limits
0.0	23	0.262	±0.020
0.5	8	.299	±0.026
1.0	8	.341	±0.020
1.5	9	.359	±0.020
2.0	8	.410	±0.050

The same information is presented graphically in Figure 2.

The complete procedure is given in Appendix I.

REFERENCES

(1) Lyon, W. L., and Weidenbaum, B., "Re: 234-5 Project Analytical Development," Document HW-11277 (1948) (Secret).

(2) Schwob, C. R., and Fred, M., "Tabulation of Chicago Analytical Methods," Document CC-2911 (1945) (Secret).

(3) Watters, J. I., "Determination of Certain Trace Impurities in Metals," Document CC-2772, pp. 52-57 (1944) (Secret).

(4) Radimer, K. J., Smiley, S. H., and Lafferty, R. H., "A Micro Method for the Determination of Gaseous Fluoride," Document A-4022 (1946) (Secret).

The experimental work is described in the following references:

Behling, G. J., <u>Hanford Works Secret Notebook</u> HW-2254-T, pp. 32-55, 61-63, 66-67, and 70.

Christopherson, E. W., <u>Hanford Works Secret Notebook</u> HW-2375-T, pp. 18-53.

Keller, C. W., <u>Hanford Works Secret Notebook</u> HW-2691-T, pp. 22-38.

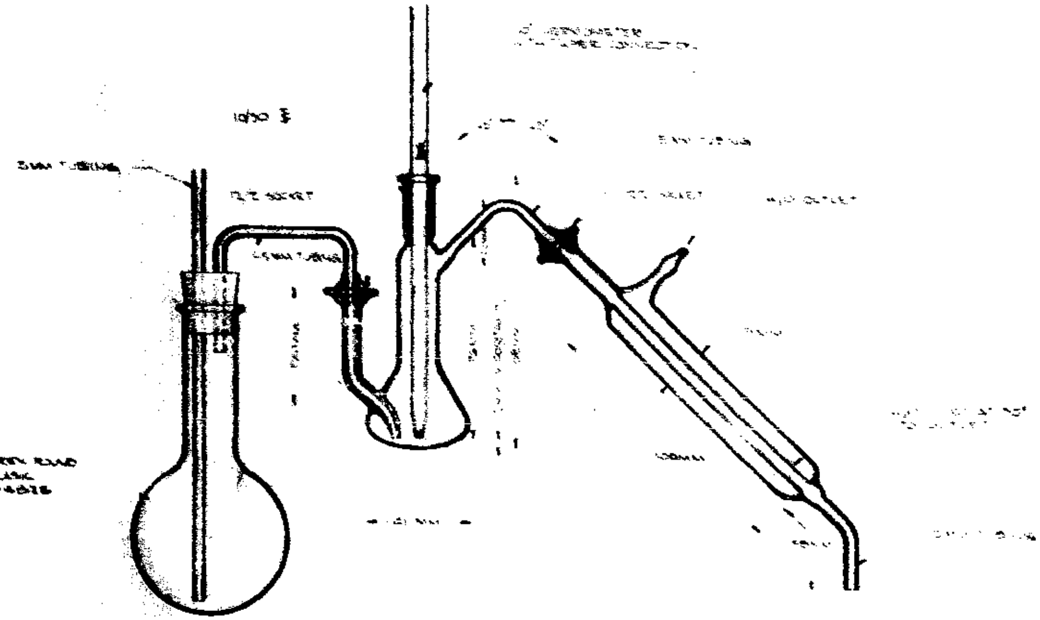
G. J. Behling

E. W. Christopherson

L. F. Kendall

[redacted]

DECLASSIFIED



H-9-1397

HANFORD WORKS

MICRO HYDROFLUO
ACID STILL UN

H-9-

DECLASSIFIED

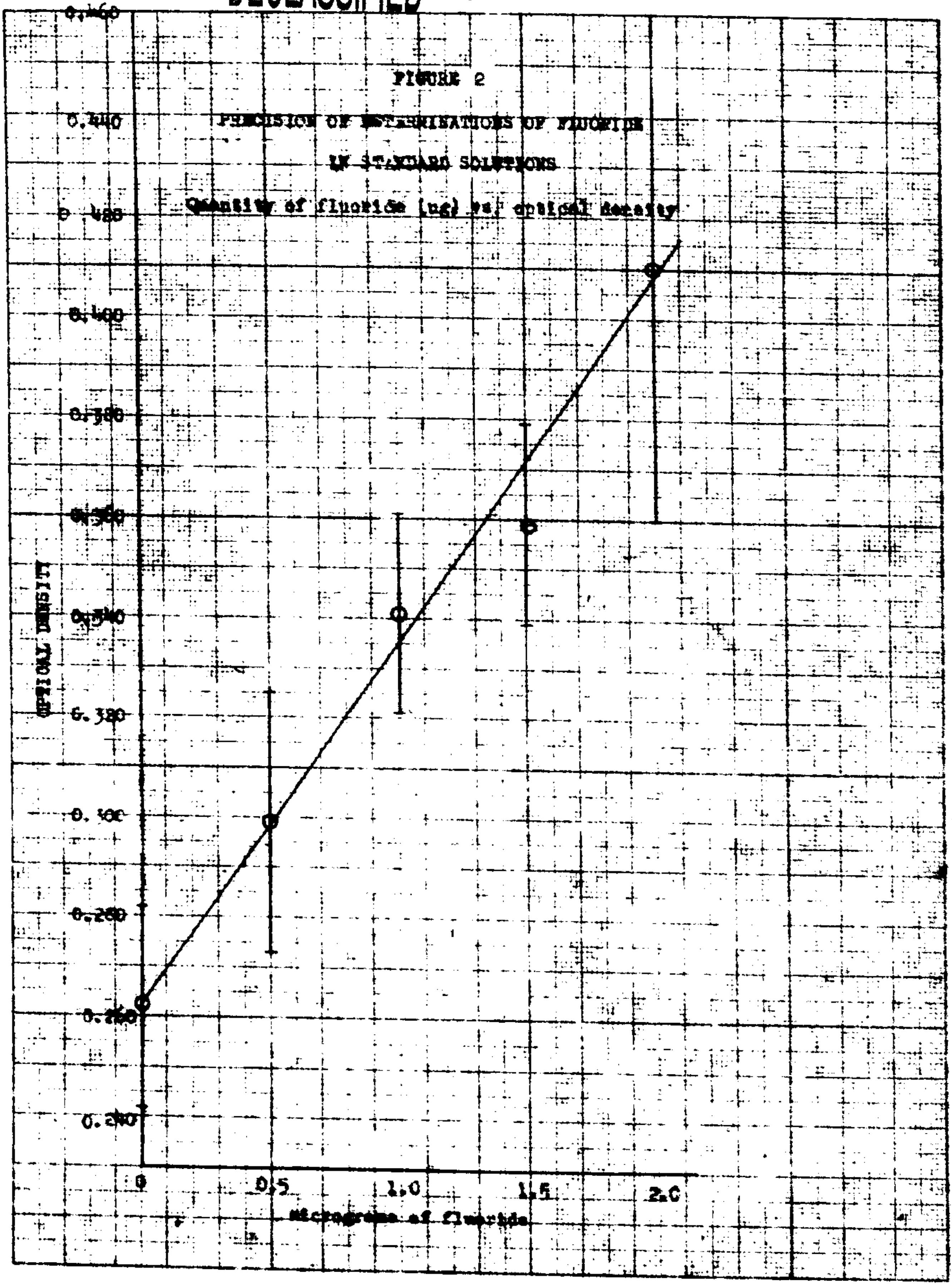


FIGURE 2

PRECISION OF DETERMINATIONS OF FLUORIDE
IN STANDARD SOLUTIONS

Quantity of fluoride (ug) vs. optical density

[redacted]

APPENDIX I

PROCEDURE

Safety Precautions

1. Follow general laboratory safety rules pertaining to hazardous materials.
2. Perchloric acid is a hazardous chemical; use extreme caution to avoid contact between the acid and rubber gloves or tubing.

Applicability

The method is applicable to samples containing acid-soluble fluoride in the range of 0.25 - 2.5 micrograms. At one microgram the accuracy is within a factor of two of the amount present.

Chemicals and Solutions Required

1. Perchloric acid, 57%.
2. Sodium hydroxide, 0.5%.
3. Acetone-hydrochloric acid mixture; mix 50 ml. of 2 N hydrochloric acid with 200 ml. of acetone.
4. Fluoride standard; dissolve 1.105 g. of sodium fluoride (dried at 110°C.) in 100 ml. of distilled water and transfer to a polyethylene bottle. For use, dilute 100 μl. to 50 ml. with distilled water.
5. Zirconium reagent suspension; add 0.100 g. zirconium reagent (see preparation page 13) to 100 ml. of distilled water containing one drop of Aerosol, and stir vigorously until the suspension appears to be homogeneous.

Procedure

A. Preparation of the Calibration Curve

A new calibration curve must be prepared for each new preparation of zirconium p-dimethylaminoazophenylarsonate and of the acetone-hydrochloric acid mixture.

1. Deliver into separate 50 ml. silica crucibles containing 5 ml. of water, 0, 50, 100, 150, and 200 microliters of freshly prepared fluoride standard solution. The crucible containing no fluoride will serve as a blank.
2. Proceed with the color development as described in steps 9-20 below, omitting step 18.
3. Plot on cross section graph paper, the optical density of each solution as ordinate against the amount of fluoride in micrograms in each solution. Draw a smooth curve through the points.

[redacted]

B. Analysis of the Sample

1. See that the distillation flask contains several soft glass beads; place 5-10 ml. of water in the steam generator; and place a 50 ml. silica crucible containing 0.2 ml. of water under the condenser tip so that the tip is beneath the surface of the water.
2. Put a sample to contain about 0.5 to 1 microgram of fluoride in the flask through the thermometer opening. Insert the thermometer.
3. Add 2 ml. of 1:10 perchloric acid cautiously through the steam inlet.
4. When gas evolution has ceased, slowly add 200 µl. of 57% perchloric acid.
5. Repeat step 4 nine times.
6. Heat both flasks so that steam begins to bubble into the acid when the temperature of the latter is 135°C.
7. Raise temperature gradually so that after 5 ml. of distillate has been collected the temperature of the acid is 140°C.
8. Turn off heater on distillation flask, lower the crucible and continue to pass steam until the temperature is 120°C.
9. Remove the crucible and add 200 µl. of 0.5% sodium hydroxide to it; place on a steam bath and evaporate to dryness.
10. Dissolve the residue in 500 µl. of water.
11. While stirring the zirconium reagent suspension vigorously, remove 200 µl. and add to the crucible.
12. Add 300 µl. of concd. hydrochloric acid. Swirl to mix, and let stand for 30 min.
13. Filter the solution through a 3 ml. fine porosity sintered glass filter into a 5 ml. volumetric flask.
14. Wash the crucible with 500 µl. of acetone-hydrochloric acid mixture and filter into the flask.
15. Repeat step 14 four times.
16. Dilute the filtrate to volume with acetone-hydrochloric acid mixture, mix thoroughly, and transfer the liquid into an absorption cell.
17. Measure the optical density of the solution at 500 mµ.
18. Determine the amount of fluoride present by reference to the calibration curve.

19. Convert the results to parts of fluoride per million of plutonium by dividing the number of micrograms of fluoride by the sample weight in grams.

20. Disconnect the steam generator from the distillation flask and replace with the waste removal line. Remove the residual acid from the still and flush by holding a beaker containing 5-10 ml. of water under the condenser tip.

Preparation of Zirconium Reagent

1. Mix 90 ml. of ethanol and 10 ml. of conc. hydrochloric acid in a 250 ml. beaker.

2. Add 2.5 gms. of p-dimethylaminoazophenylarsonic acid and place the beaker on a hot plate. Heat to 60°C. while agitating with a mechanical stirrer.

3. Dissolve 1.0 gm. of zirconyl chloride in 100 ml. of 1 N hydrochloric acid. Add this solution slowly with vigorous stirring to the mixture in the beaker.

4. Continue stirring for 1 hour, maintaining the temperature at 60°C. Let cool to room temperature.

5. Transfer part of the slurry to a 50 ml. centrifuge tube and centrifuge until the supernatant is clear. Remove the supernatant and discard.

6. Repeat step 5 until all of the slurry has been centrifuged.

7. Wash the cake by adding 25 ml. of 2 N hydrochloric acid and stirring vigorously for 5 minutes. Centrifuge, remove and discard the supernatant.

8. Repeat step 7.

9. Repeat steps 7 and 8 using 2 N hydrochloric acid which has been heated to 50°C.

10. Repeat steps 7 and 8 until five successive washes are of equal color.

11. Wash twice by adding two 25 ml. portions of distilled water and stirring for one minute; centrifuge, remove and discard the supernatant.

12. Repeat step 11 four times, using two portions each of ethanol and of ether.

13. Remove the cake from the tube with a spatula and transfer to a large piece of filter paper. Let dry in air.

14. Transfer the dried product to a mortar and grind.

[redacted]

15. Transfer the product to a 200 mesh sieve and brush the powder on the sieve.

16. Regrind the particles which do not pass the sieve and repeat step 15.

17. Repeat step 16 until all of the product has passed the sieve. Transfer to a two ounce screw cap vial.

[redacted]