Designation: C 1022 – 93

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Methods for Chemical and Atomic Absorption Analysis of Uranium-Ore Concentrate[1]

This standard is issued under the fixed designation C 1022; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover procedures for the chemical and atomic absorption analysis of uranium-ore concentrates to determine compliance with the requirements prescribed in Specification C 967.

1.2 The analytical procedures appear in the following order:

	Sections
Uranium by Ferrous Sulfate Reduction—Potassium Dichromate Titrimetry	9 to 16
Nitric Acid-Insoluble Uranium	17 to 25
Extractable Organic Material	26 to 33
Arsenic by Diethyldithiocarbamate (Photometric Method)	34 to 43
Carbonate by CO_2 Gravimetry	44 to 50
Fluoride by Ion-Selective Electrode	51 to 58
Halides by Volhard Titration	59 to 66
Moisture by Loss of Weight at 110°C	67 to 73
Phosphorus by Spectrophotometry	74 to 82
Silicon by Gravimetry	83 to 89
Thorium by the Thorin (Photometric) Method	90 to 98
Calcium, Iron, Magnesium, Molybdenum, Titanium, and Vanadium by Atomic Absorption Spectrophotometry	99 to 108
Potassium and Sodium by Atomic Absorption Spectrophotometry	109 to 118
Boron by Spectrophotometry	119 to 128

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Sections 7, 39, and Note 16.

2. Referenced Documents

2.1 *ASTM Standards:*

C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride[2]

C 859 Terminology Relating to Nuclear Materials[2]

C 967 Specification for Uranium Ore Concentrate[2]

D 1193 Specification for Reagent Water[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology C 859.

4. Significance and Use

4.1 The test methods in this standard are designed to show whether a given material meets the specifications prescribed in Specification C 967.

4.2 Because of the variability of matrices of uranium-ore concentrate and the lack of suitable reference or calibration materials, the precision and bias of these test methods should be established by each individual laboratory that will use them. The precision and bias statements given for each test method are those reported by various laboratories and can be used as a guideline.

4.3 Instrumental test methods such as X-ray fluorescence and emission spectroscopy can be used for the determination of some impurities where such equipment is available.

5. Interferences

5.1 Interferences are identified in the individual test methods.

5.2 Ore concentrates are of a very variable nature; therefore, all interferences are very difficult to predict. The individual user should verify the applicability of each procedure for specific ore concentrates.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of

[1] These test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved Nov. 15, 1993. Published February 1994. Originally published as C 1022 – 84. Last previous edition C 1022 – 84 (1990).

[2] *Annual Book of ASTM Standards*, Vol 12.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

7. Precautions

7.1 Proper precautions should be taken to prevent inhalation or ingestion of uranium during sample preparation and any subsequent sample analysis.

8. Sampling

8.1 Collect samples in accordance with Specification C 967.

8.2 Special requirements for subsampling are given in the individual test methods.

URANIUM BY FERROUS SULFATE REDUCTION—POTASSIUM DICHROMATE TITRIMETRY

9. Scope

9.1 This test method covers the determination of uranium in uranium-ore concentrates.

10. Summary of Test Method

10.1 A sample for analysis is taken according to a time-weighing procedure and dissolved in a mixture of nitric and sulfuric acids. Weighed solution aliquots are then taken for analysis.

10.2 An excess of ferrous sulfate is used to reduce uranium(VI) to uranium(IV) in a concentrated phosphoric acid solution containing sulfamic acid. The excess iron is subsequently oxidized by nitric acid in the presence of molybdenum(VI). After dilution with water and addition of vanadium(IV), the determination is completed by titrating with standard potassium dichromate solution to a potentiometric end point **(1, 2, 3)**.[6]

11. Interferences

11.1 Interference may be caused by silver, tin(II), arsenic(III), mercury, antimony(III), vanadium, manganese, molybdenum in the presence of nitric acid, platinum, palladium, osmium, iridium, ruthenium, and halides other than complexed fluorides **(1, 3, 4, 5)**.

12. Apparatus

12.1 *Buret*, Class A, 50 mL or 100 mL, with a bulb reservoir.

12.2 *pH Meter*, with a platinum wire electrode and a calomel reference electrode.

12.3 *Magnetic Stirrer*.

12.4 *Timer*.

12.5 *Steam Bath*.

13. Reagents

13.1 *Hydrofluoric Acid* (HF, 48 %).

13.2 *Nitric Acid* (HNO_3, sp gr 1.42)

13.3 *Perchloric Acid* ($HClO_4$, 62 %)

13.4 *Sulfuric Acid* (9 *M*)—Add 500 mL H_2SO_4 (sp gr 1.84) to 500 mL or iced water with constant stirring. Cool and dilute to 1 L with water.

13.5 *Ferrous Sulfate Solution* (1.0 *M*)—Add 100 mL of sulfuric acid (H_2SO_4, sp gr 1.84) to 750 mL of water as the solution is stirred. Add 278 g of $FeSO_4 \cdot 7H_2O$ and dilute the solution to 1 L with water. Discard after 2 weeks.

13.6 *Nitric Acid* (8 *M*) *Sulfamic Acid* (0.15 *M*) - *Ammonium Molybdate* (4 g/L) *Solution*—Dissolve 4 g of $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ in 400 mL of water, and add 500 mL of HNO_3 (sp gr 1.42). Mix, then add 100 mL of 1.5 *M* sulfamic acid solution (13.10), and mix.

13.7 *Phosphoric Acid* (H_3PO_4, 85 %).

13.8 *Potassium Dichromate* (20 g/L)—Dissolve 2 g of $K_2Cr_2O_7$ in 100 mL of water.

13.9 *Potassium Dichromate Solution, Standard* (0.02500 *N*)–Dissolve 1.2258 g of potassium dichromate[7] ($K_2Cr_2O_7$) that has been dried for 1 h at 100°C in water, then dilute to 1 L with water in a volumetric flask. Mix thoroughly and record the temperature of the solution.

13.10 *Sulfamic Acid Solution* (1.5 *M*)—Dissolve 146 g of NH_2SO_3H in water and dilute to 1 L with water, then filter.

13.11 *Vanadyl Sulfate* ($VOSO_4 \cdot 2H_2O$) *Crystals*—A highpurity reagent free of V^{3+} and V^{5+}, Vanadium^{+3}, and Vanadium^{+5} shall be used.

14. Procedure

14.1 Break the seal on the sample container (if packaged under vacuum) and mix contents for 5 to 10 min in a mixer.

14.2 Open the container, record the time of opening, and weigh accurately about 3 g of sample into a weighing dish.

14.3 Record the sample weight to the nearest 0.1 mg and the length of time taken to complete the sampling-weighing process; then wait this length of time and reweigh the sample.

14.4 Transfer the sample to a 400-mL beaker and wet it with water.

14.5 Add 15 mL HNO_3, 20 mL 9 *M* H_2SO_4, and 3 mL of $HClO_4$ (62 %). Cover the beaker and take to fumes on a hot plate until the sample is dissolved.

14.6 Allow to cool, add 2 mL HF and heat to fuming.

14.7 Cool and transfer the solution, using a small amount of water, to a 125-mL plastic bottle tared to the nearest 1 mg. Dilute to about 100 mL with water.

14.8 Weigh the bottle and contents to the nearest 1 mg and mix contents thoroughly.

14.9 Transfer a portion (weighed to the nearest 0.1 mg) of the sample solution containing 100 to 150 mg of uranium to a 400-mL beaker.

14.10 Rinse down the sides of the beaker with about 10 mL of water and place a magnetic stirring bar in the solution.

NOTE 1—The volume of the final solution must not exceed 15 mL.

14.11 Add the following reagents in the order given, mixing after each addition: 5 mL of 1.5 *M* sulfamic acid solution, 40

[6] The boldface numbers in parentheses refer to the list of references at the end of these test methods.

[7] NBS SRM 136c or its equivalent has been found suitable.

mL of H_3PO_4 containing 2 drops of 20 g/L $K_2Cr_2O_7$ solution, and 5 mL of 1.0 *M* $FeSO_4$ solution.

NOTE 2—Carefully pipet the $FeSO_4$ solution addition directly into the phosphoric acid-sulfamic acid solution.

14.12 Wait a minimum of 60 s, adjust the temperature of the solution to 35 to 40°C, then using the reagent to wash down the inner walls of the beaker, pipet 10 mL of the reagent prescribed in 13.6.

14.13 Stir for 2.5 min and let stand for an additional 0.5 min to allow bubbles to disperse.

NOTE 3—Because this reaction is time and temperature dependent, carefully observe the times specified.

14.14 Add 100 mL of water and approximately 100 mg of $VOSO_4 \cdot 2H_2O$ roughly measured with a small spatula.

14.15 Start stirring rapidly, then insert the platinum and calomel electrodes. Titrate rapidly with 0.02500 *N* $K_2Cr_2O_7$ solution until a potential of 500 mV is reached. Then titrate more slowly to a sharp break in potential that will occur near 590 mV, allowing no more than 7 min before completion of the titration.

14.16 Record the volume of titrant to the nearest 0.01 mL and the solution temperature.

15. Calculation

15.1 Calculate the percentage of uranium content, *U*, on a sample basis as follows:

$$U = \frac{(T \times V)\, W_S \times 100}{W_F \times W_A} \tag{1}$$

where:
T = uranium equivalent to 1 mL of titrant, g,
V = volume of titrant, corrected for the differences between the temperature recorded in 14.16 and the temperature recorded in 13.9,
W_S = weight of total sample solution (see 15.1.1),
W_F = weight of solid sample (see 15.1.2), and
W_A = weight of sample aliquot taken for analysis (see 14.9), g.

15.1.1 Calculate the weight of the total sample solution, W_S, as follows:

$$W_S = W_4 - W_3 \tag{2}$$

where:
W_4 = weight of sample solution plus the container (see 14.8), g, and
W_3 = weight of container alone (see 14.7), g.

15.1.2 Calculate the weight of solid sample, W_F, as follows:

$$W_F = W_1 - (W_2 - W_1) \tag{3}$$

where:
W_1 = initial weight of sample, g, and
W_2 = final weight of sample (see 14.3), g.

16. Precision and Bias

16.1 *Precision*—A relative standard deviation of 0.08 % has been reported (see 4.2).

16.2 *Bias*—For information on the bias of this test method see 4.2 and Refs **(1-5)**.

NITRIC ACID-INSOLUBLE URANIUM

17. Scope

17.1 This test method covers the determination of that quantity of uranium in uranium-ore concentrate that is not soluble in nitric acid.

18. Summary of Test Method

18.1 A sample of ore concentrate is digested in 10 *M* nitric acid at 95 to 100°C for 1 h. The slurry is filtered and the residue washed with 1 *M* nitric acid until the filtrate gives a negative test for uranium. The washed residue is then dried and ignited at 1000 ± 25°C for 1 h. The uranium content is determined on the ignited residue by spectrophotometry.

19. Interference

19.1 At the specification limit for nitric acid insoluble uranium usually established for uranium-ore concentrates, interference effects are insignificant.

20. Apparatus

20.1 *Digestion Flask*, 500-mL, with side entry tube and attached reservoir.
20.2 *Stirring Apparatus*, with sleeve-type stirrer.
20.3 *Heating Mantle*, 250-W, controlled by a variable transformer.
20.4 *Büchner Funnel*.
20.5 *Porcelain Crucibles*, 40-mL.
20.6 *Muffle Furnace*.
20.7 *Filter Paper*, [8] of medium porosity.
20.8 *Spectrophotometer*, with 1-cm cells that are in accordance with Practice E 60.

21. Reagents

21.1 *Nitric Acid* (10 *M*)—Dilute 62.5 mL of HNO_3 (sp gr 1.42) to 100 mL with distilled water.
21.2 *Nitric Acid* (1 *M*)—Dilute 62.5 mL of HNO_3 (sp gr 1.42) to 1 L with distilled water.
21.3 *Sodium Hydroxide* (100 g/L)—Dissolve 10 g of NaOH in 100 mL of water.
21.4 *Hydrogen Peroxide* (H_2O_2, 30 %).
21.5 *Hydrochloric Acid* (HCl, sp gr 1.19).
21.6 *Hydrofluoric Acid* (HF, 48 %).
21.7 *Sulfuric Acid* (9 *M*)—Add 500 mL H_2SO_4 (sp gr 1.84) to 500 mL of iced water with constant stirring. Cool and dilute to 1 L with water.

22. Procedure

22.1 Weigh a 50.0 ± 0.1-g sample directly into the digestion flask.

22.2 Place the flask in the heating mantle and adjust the support ring so that the joints of the flask and sleeve stirrer are engaged, and the stirrer blades turn freely but just clear the bottom of the flask.

22.3 Transfer 95 mL of 10 *M* nitric acid to a 250-mL beaker and heat between 95 to 100°C.

[8] Whatman brand No. 40 or its equivalent has been found suitable.

22.4 Slowly transfer the heated nitric acid solution to the digestion flask through the entry side tube with the stirrer turning.

NOTE 4—The stirrer is started before the acid is added to prevent material from sticking to the flask.

22.5 Align a thermometer in such a manner that the mercury chamber of the thermometer is immersed in the stirring slurry, but adequately clears the turning stirrer blades.

22.6 Quickly bring the sample to 97°C and digest between 95 to 100°C for 1 h while stirring. (Measure the 1-h digestion time after the temperature of the slurry has reached 97°C.)

22.7 Turn off the variable transformer, but allow the stirrer to continue turning.

22.8 Remove the thermometer and carfully rinse with water all slurry that adheres to it.

22.9 Wipe the immersed portion of the thermometer with one fourth of a circle of filter paper and transfer the paper to a prepared Büchner funnel fitted with a filter paper.

22.10 Add 10 mL of paper pulp to the slurry and continue stirring for about 5 min.

22.11 Turn off the stirrer, then lower the flask and mantle.

22.12 Carefully wash the slurry that adheres to the stirrer shaft and blades into the flask with water.

22.13 Wipe the shaft and blades with one fourth of a circle of filter paper and transfer the filter paper to the Büchner funnel.

22.14 Filter the slurry through the Büchner funnel and wash contents of the flask into the funnel.

22.15 Wash the residue with 1 *M* nitric acid until a 10-mL portion of the filtrate shows no detectable yellow color when made basic with sodium hydroxide and after a few drops of H_2O_2 (30 %) have been added as a color developer.

22.16 Wash the residue several times with water after a negative test is obtained.

22.17 Draw air through the filter until the residue and filter pad are dry.

22.18 Scrape the residue and paper into a preignited (1000°C) tared 40-mL crucible, place on a hot plate and slowly char off the organic material.

22.19 Ignite the residue for 1 h at 1000°C in a muffle furnace.

22.20 Cool the crucible in a desiccator and weigh.

22.21 Calculate the percentage of solids in accordance with 24.1.

NOTE 5—If the percentage of solids (insoluble residue) is greater than 0.1 %, grind and mix the residue and determine the total milligrams of uranium in the residue by the photometric procedure in 23.1-23.10.

23. Photometric Procedure for Uranium

23.1 Transfer the ground, blended residue from 22.20 to a 100-mL beaker.

23.2 Add 10 mL of water and 10 mL of HCl (sp gr 1.19), cover, and boil for 10 min.

23.3 Add 5 mL of HNO_3 (sp gr 1.42) and boil until fuming of NO_2 ceases. Remove cover glass.

23.4 Add 5 mL of 9*M* H_2SO_4 and 2 mL of HF (48 %), then heat to dryness on the hotplate. Bake to fume off remaining H_2SO_4 and cool.

23.5 Wash down sides of beaker with water and add 5 mL of HNO_3.

23.6 Cover with a watchglass and digest for approximately 10 min near the boiling point.

23.7 Quantitatively transfer the solution to a 250-mL volumetric flask. Add 25 mL of NaOH solution and a few drops of H_2O_2. Make up to mark with water and mix.

NOTE 6—The solution must be basic for yellow sodium peruranate color to develop.

23.8 Measure the absorbance of the solution in a spectrophotometer at 425 nm in a 1-cm cell using a blank as reference. The blank is prepared by diluting 25 mL of NaOH, plus a few drops of H_2O_2, to 250 mL with water.

23.9 Prepare a calibration curve covering the range from 0 to 50 mg of uranium from aliquots of a standard uranium solution. Proceed as in 23.5-23.8. Plot the milligrams of uranium against absorbance readings.

23.10 Determine the total milligrams of uranium in the sample solution from the calibration curve.

NOTE 7—If the sample solution falls outside the calibration range, dilute a portion with the reference-blank solution and read again.

24. Calculation

24.1 Calculate the percentage of insoluble residue, *R*, present as follows:

$$R = \frac{R_w \times 100}{S_w} \quad (4)$$

where:
R_w = weight of residue (see 22.20), g, and
S_w = weight of samples, g.

24.2 If the insoluble residue exceeds 0.1 %, calculate the percentage of nitric acid-insoluble uranium, U_N, and present as follows:

$$U_N = \frac{U}{S_w \times 10} \quad (5)$$

where:
U = uranium content calculated in 23.10, mg, and
S_w = weight of sample, g.

24.3 Calculate the percentage of nitric acid-insoluble uranium, U_u, on a uranium basis as follows:

$$U_u = \frac{U_N \times 100}{U_s} \quad (6)$$

where:
U_N = nitric acid-insoluble residue present (see 24.2), %, and
U_s = uranium in sample, %.

25. Precision and Bias

25.1 *Precision*—A relative standard deviation for this test method has been reported as 10 % at the 0.2 % HNO_3 insoluble uranium level (see 4.2).

25.2 *Bias*—For information on the bias of this test method see 4.2.

EXTRACTABLE ORGANIC MATERIAL

26. Scope

26.1 This test method is used to determine the extractable organic material in uranium-ore concentrates. It is recognized that certain water-soluble organic materials, such as flocculating agents, are not measured by this test method.

27. Summary of Test Method

27.1 This test method consists of a dual extraction using trichlorofluoromethane on the solid uranium-ore concentrate sample and chloroform on a subsequent nitric acid solution of the sample. Each of the extractants is evaporated to measure the amount of organic material extracted.

28. Interferences

28.1 At the specification limit for extractable organic material established for uranium-ore concentrations, and within the scope of this test method, interferences are insignificant.

29. Apparatus

29.1 *Soxhlet Extraction Apparatus*—The trichlorofluoromethane extraction is done in a Soxhlet extraction apparatus. Construct as follows (see Fig. 1):

29.1.1 Modify a medium Soxhlet extraction tube so that the sidearm siphon is about 2 cm high, therefore, reducing the volume of solvent needed. Insert a 3 to 4-cm long, 25-mm outside diameter glass tube upright into the extraction tube in such a manner that an extraction thimble may be placed on it.

29.1.2 Connect a 250-mL Florence flask, that has a 24/40 ground-glass joint on the lower end to the top of the extraction tube. A250-mL heating mantle connected to a 7.5-A variable transformer shall be used to heat this.

29.1.3 Connect a Friedrichs condenser, that has a 45/50 ground-glass joint on the lower end, to the top of the extraction tube. Turn this side of the condenser upward, and fuse the outer member of a 24/40 ground-glass joint to it.

29.1.4 Connect a Graham condenser, that has a 24/40 ground-glass joint on the lower end, to the modified sidearm of the Friedrichs condenser. Unless the relative humidity is low, insulate the Graham condenser to prevent the condensation of water on the outside surface that might seep through the joint to the Friedrichs condenser. Foam insulation 1 cm thick may be used for this purpose. The Graham condenser is cooled with cold water from a water bath cooler, and may be required when trichlorofluoromethane is used for the extraction.

29.2 *Heat gun* (hot-air electric dryer), may be used to evaporate the solvent in procedure 31.6 or 31.15.

29.3 *Extraction Thimbles*.

29.4 *Filter Paper*. [9]

29.5 *Phase Separator Paper*. [10]

30. Reagents

30.1 *Trichlorofluoromethane* (or 1,1,2 trichlorotrifluoroethane)—Whenever a new supply is used, it should be checked for nonvolatile residue. Evaporate 100.0 mL just to dryness in a weighted platinum dish, cool to room temperature, and reweigh the dish. If there is any residue, either make the appropriate blank correction or distill the solvent before use to remove the nonvolatile impurities.

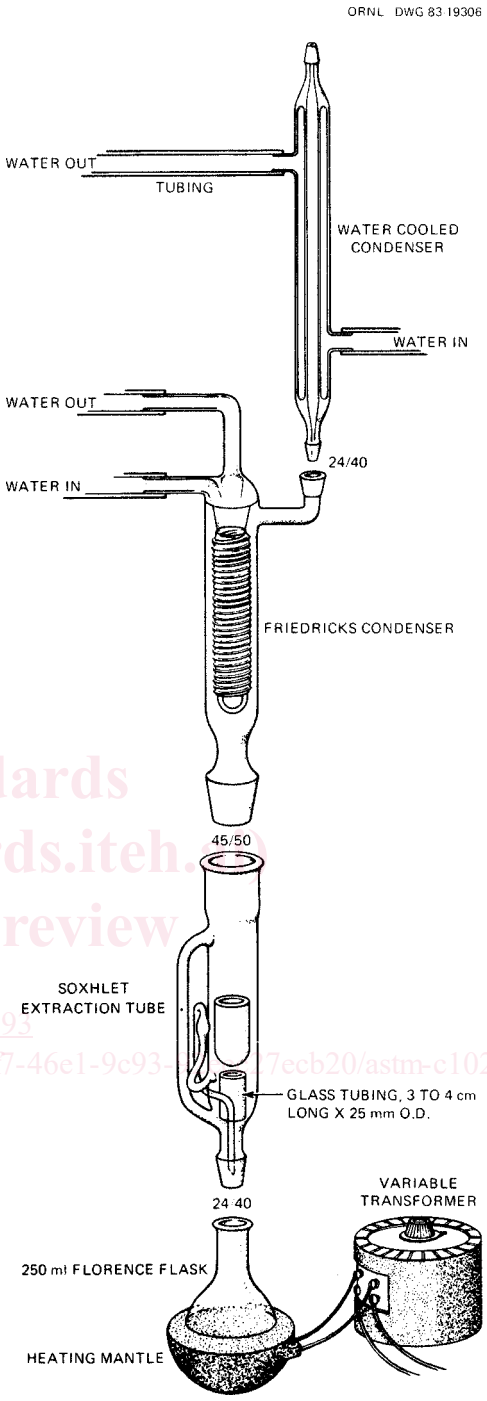


FIG. 1 Freon Extraction Unit

30.2 *Nitric Acid* (1 + 1)—Mix equal volumes of concentrated (sp gr 1.42) reagent grade HNO_3 and distilled water.

30.3 *Chloroform*—Whenever a new supply of chloroform is to be used, it should be checked for nonvolatile residue as described in 30.1.

[9] Whatman brand size 33 by 94 mm has been found suitable.

[10] Whatman IPS has been found suitable.

31. Procedure

31.1 Weigh 50.0 g of well-mixed, undried uranium-concentrate sample and transfer to an extraction thimble while tapping the thimble on a table top to compact and level the sample.

31.2 Place a plug of glass wool in the thimble above the sample. Support the thimble on the glass tube in the Soxhlet extraction tube so that when solvent condenses on the lower tip of the Friedrichs condenser, it will drop into the thimble.

31.3 Connect the extraction tube to the bottom of the Friedrichs condenser that is in series with the Graham condenser. Turn on the tap water coolant to the condensers.

NOTE 8—Tap water may be used in cooling both condensers if the amount of reagent lost during the refluxing (see 31.5) is not greater than 10 % of the volume added in 31.4. If the tap water is too warm, then the Graham condenser must be cooled by the refrigerated water cooler, or an ice-cooled condenser may be used in place of the Graham condenser.

31.4 Add a piece of sintered glass or several glass boiling beads and then 120 to 125 mL trichlorofluoromethane to the 250-mL Florence flask. Attach the flask to the Soxhlet extraction tube.

NOTE 9—If the humidity is high and results for extractable organic material on recent lots from the same producer have been less than 0.05 %, 1,1,2 trichlorofluoroethane may be used in place of trichlorofluoromethane to reduce any difficulty caused by the condensation of moisture.

31.5 Place the heating mantle below the Florence flask, connect to the variable transformer set at 55 to 60 V, and allow the reagent to reflux rapidly for 3 ½ to 4 h.

31.6 Pour the refluxed reagent into a weighed (W_1 in grams) platinum dish, and evaporate in a hood. An infrared lamp or hot air stream from a heat gun may be used.

NOTE 10—Exercise care in this evaporation. If a heat source is used, adjust the rate of heat input and velocity of air across the dish so that no sample will be mechanically lost. If a heat gun is used, the amount and temperature of the air directed against the sample are especially critical because the high rate of evaporation is likely to lower the temperature of the solution to the point where water will condense in the dish.

31.7 Allow the dish to come to room temperature while tilting and rotating it to spread the last few drops of solvent uniformly over the bottom.

NOTE 11—Do not allow the temperature of the dish to go below the dewpoint.

31.8 Weigh in open air at intervals on an analytical balance, recording the weight of the dish 5 min after the rate of loss has decreased to 0.5 mg/min.

NOTE 12—This weight is in grams as W_2.

31.9 Add a plastic-covered magnetic stirring bar and 100 mL of (1 + 1) nitric acid to a 400-mL beaker.

31.10 While magnetically stirring the acid, cautiously add the extracted sample from the extraction thimble. Stir until the sample is dissolved or until it is apparent that practically no more sample will dissolve.

31.11 Cool to about room temperature and transfer to a 500-mL separatory funnel. Add 100.0 mL of chloroform, stopper tightly, and shake as vigorously as possible for 60 s.

31.12 Allow the phases to separate.

NOTE 13—If emulsions form, transfer to centrifuge tubes and centrifuge to separate the phases.

31.13 Drain off the lower phase. If the lower phase is the chloroform layer, filter through a phase-separator filter paper into a graduated cylinder or narrow-neck flask. If the lower phase is the aqueous phase, drain and discard. Then filter the upper phase through a phase-separator filter paper into a graduated cylinder or narrow-neck flask.

31.14 Transfer 50.0 mL of the filtered chloroform into an ignited (900°C) platinum dish.

31.15 Place the platinum dish in a hood and evaporate until about 1 mL of chloroform remains. This evaporation may be done as described in 31.6.

31.16 Allow the dish to cool to room temperature while tilting and rotating it to spread the last few drops uniformly over the bottom.

31.17 Weigh in open air on a recording balance or at intervals on an analytical balance, recording the weight of the dish 5 min after the rate of weight loss has decreased to 0.5 mg/min.

NOTE 14—This weight is in grams as W_3.

31.18 Ignite the platinum dish at 900°C for a minimum of 30 min, cool to room temperature, and weigh.

NOTE 15—This weight is in grams as W_4.

32. Calculation

32.1 Calculate the percentage of extractable organic material, O_m, as follows:

$$O_m = \frac{100\,[(W_2 - W_1) + 2\,(W_3 - W_4)]}{S_w} \quad (7)$$

where:

W_2 = weight of platinum dish in 31.8, g,
W_1 = weight of platinum dish in 31.6, g,
W_3 = weight of platinum dish in 31.17, g,
W_4 = weight of platinum dish in 31.18, g, and
S_w = weight of sample.

33. Precision and Bias

33.1 *Precision*—A relative standard deviation for this test method has been reported as 18 % at the 0.1 % extractable organic level (see 4.2).

33.2 *Bias*—For information on the bias of this test method see 4.2.

ARSENIC BY DIETHYLDITHIOCARBAMATE (PHOTOMETRIC) METHOD

34. Scope

34.1 This test method covers the determination of arsenic in uranium-ore concentrate.

34.2 Sample aliquots containing up to 25 µg of arsenic may be analyzed by this test method.

35. Summary of Test Method

35.1 Arsenic compounds are reduced to gaseous arsine by hydrogen generated by zinc in an acid medium. The resulting mixture of gases is passed through a scrubber containing

borosilicate wool impregnated with lead acetate solution, and then into an absorption tube containing a solution of silver diethyldithiocarbamate dissolved in pyridine. Arsine reacts with this reagent to form a soluble red substance having maximum absorbance at 540 nm. The absorbance of the solution is measured spectrophotometrically and the arsenic determined by reference to a calibration curve prepared from standards.

36. Interferences

36.1 Although many samples are relatively free of interferences, cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum may interfere with the evolution of arsine and with the recovery of arsenic. The presence of any or all of these metals in a sample being analyzed must be considered as a potential source of interference and the analyst must be aware of the extent of actual interferences if any.

36.2 Hydrogen sulfide and other sulfides interfere, but commonly encountered quantities are effectively removed by the lead-acetate scrubber.

36.3 Antimony interferes by forming stibine which distills along with the arsine. Stibine reacts with the color-forming reagent to form a red compound having maximum absorbance at 510 nm. The absorbance for antimony at 540 nm is about 8 % of that of arsenic for equal concentrations.

37. Apparatus

37.1 *Arsine Generator, Scrubber, and Absorber*. [11]

37.2 *Spectrophotometer*, with 1-cm cells in accordance with Practice E 60.

38. Reagents

38.1 *Arsenic Solution, Standard I* (1 mg As/mL)—Dissolve 1.320 g of arsenic trioxide (As_2O_3) (**Warning**, Note 16) dried for at least 1 h at 110°C, in 10 mL of 10 *M* sodium hydroxide (NaOH) solution and dilute to 1 L with water. This solution is stable.

NOTE 16—**Warning:** Arsenic trioxide is extremely toxic. Avoid ingestion.

38.2 *Arsenic Solution, Standard II* (10 µg As/mL)—Dilute 5 mL of arsenic standard solution I to 500 mL with water in a volumetric flask.

38.3 *Arsenic Solution, Standard III* (1 µg As/mL)—Dilute 10 mL of arsenic standard solution II to 100 mL with water in a volumetric flask. Prepare freshly before each use.

38.4 *Hydrochloric Acid* (HCl, sp gr 1.19)—Use analyticalgrade acid with an arsenic content no greater than 0.01 µg/mL.

38.5 *Lead Acetate Solution* (100 g/L)—Dissolve 10 g of lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$) in water and dilute to 100 mL. Store reagent in a tightly stoppered container.

38.6 *Nitric Acid* (1 + 1)—Add 250 mL of nitric acid (HNO_3, sp gr 1.42) to 250 mL of water and mix.

38.7 *Perchloric Acid*—($HClO_4$, 62 %), use analytical-grade acid with an arsenic content no greater than 0.01 µg/mL.

38.8 *Potassium Iodide Solution* (150 g/L)—Dissolve 15 g of KI in water and dilute to 100 mL. Store in an amber bottle.

38.9 *Silver Diethyldithiocarbamate - Pyridine Solution* (5 g/L)—Dissolve 0.5 g of silver diethyldithiocarbamate in 100 mL of pyridine. This solution is stable for at least several months when stored in an amber bottle.

38.10 *Sodium Hydroxide Solution* (420 g/L)—Dissolve 42 g of NaOH pellet in water and dilute to 100 mL.

38.11 *Stannous Chloride - Hydrochloric Acid Solution* (400 g/L)—Dissolve 40 g of arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL of HCl (sp gr 1.19). Add a few small pieces of mossy tin.

38.12 *Zinc* (*Granular*, 20 mesh)—Arsenic content must not exceed 1 µg of arsenic per gram of zinc.

38.13 *Sulfuric Acid* (H_2SO_4, sp gr 1.84)—Use analyticalgrade acid with an arsenic content no greater than 0.01 µg/mL.

39. Precautions

39.1 Take proper precautions to prevent inhalation or ingestion of arsine, arsenic, or pyridine during the analysis. Furthermore, do not allow the pyridine to contact the skin.

40. Calibration

40.1 Clean all glassware before use by rinsing first with hot (1 + 1) HNO_3, then with water. Also, rinse the absorbers with acetone and air dry.

40.2 Prepare a blank and a series of standards by pipetting appropriate volumes of arsenic standard solution III (**Caution**, Note 16) into arsine-generating flasks. The standards should cover the range from 0 to 25 µg of arsenic.

40.3 Dilute each standard and blank to approximately 25 mL.

40.4 Add successively to each flask, with thorough mixing after each addition, 5 mL of HCl (sp gr 1.19), 2 mL of KI solution, and 8 drops of $SnCl_2$ solution. Let stand about 15 min to allow the arsenic to completely reduce to the tirvalent state.

40.5 Place in each scrubber a plug of borosilicate wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL of silver diethyldithiocarbamate - pyridine solution to each absorber, then add glass beads to the absorbers until the liquid just covers them.

40.6 Disconnect each generator, add 3 g of zinc, and reconnect immediately.

40.7 Allow 30 min for complete evolution of arsine. Warm the generator flasks for a few minutes to make sure all arsine is released.

40.8 Pour the solutions from the absorbers directly into clean spectrophotometer cells and, within 30 min, measure the absorbance of each at 540 nm using water in the reference cell.

40.9 Prepare a calibration curve by plotting micrograms of arsenic against the corresponding absorbance of each standard after correcting for the blank.

41. Procedure

41.1 Clean all glassware by rinsing with hot (1 + 1) HNO_3 before use.

41.2 Weigh 1 g of uranium-ore concentrate into a 250-mL

[11] An adequate system can be obtained from laboratory supply houses.

Erlenmeyer flask. Add 12 mL of H_2SO_4, 5 mL of $HClO_4$, and 5 mL (1 + 1) HNO_3. Boil the sample on a hot plate until the fumes of the H_2SO_4 just begin to come off. Cool, transfer to a 100-mL volumetric flask, and dilute to volume with water.

41.3 Pipet an aliquot of sample containing less than 25 µg of arsenic (25 mL maximum) from the volumetric flask into a generating flask and dilute to approximately 25 mL.

41.4 Proceed as directed in 40.4-40.8.

41.5 Determine the reagent blank by repeating the procedure in 41.1-41.4, but omit the sample in 41.2 and take the same aliquot in 41.3 as was used for the sample.

41.6 Subtract the reagent blank from the absorbance of the sample aliquot, then determine the amount of arsenic in the sample aliquot by reference to the calibration curve prepared in 40.9.

42. Calculation

42.1 Calculate the percentage of arsenic concentration, *A*, in the sample as follows:

$$A = \frac{W}{G \times V \times 100} \quad (8)$$

where:

W = amount of arsenic in sample aliquot as determined from the calibration curve, µg,
G = amount of sample taken, g, and
V = volume of aliquot taken in 41.3, mL.

42.2 Calculate the percentage of arsenic concentration, A_u, in the sample on a uranium basis as follows:

$$A_u = \frac{A \times 100}{U} \quad (9)$$

where:

A = arsenic concentration calculated in 42.2, %, and
U = uranium in sample, %.

43. Precision and Bias

43.1 *Precision*—A relative standard deviation has been reported as 4 % at the 0.1 % arsenic level (see 4.2).

43.2 *Bias*—For information on the bias of this test method see 4.2.

CARBONATE BY CO_2 GRAVIMETRY

44. Scope

44.1 This test method covers the determination of 0.1 to 3 % carbonate in uranium-ore concentrate.

44.2 The concentration range can be extended by taking smaller sample weights.

45. Summary of Test Method

45.1 The carbonate in the sample is decomposed with hydrochloric acid and evolved as carbon dioxide. The incoming air is dried and the CO_2 is removed by passing it through NaOH and anhydrous calcium sulfate ($CaSO_4$). The evolved gases are scrubbed in H_2SO_4 to remove moisture and passed through a tower of manganese dioxide and zinc metal to remove any SO_2 or H_2S formed. The evolved gas is then absorbed by NaOH in a Nesbitt bulb and determined gravimetrically **(6)**.

46. Apparatus

46.1 *Carbonate Apparatus*, (see Fig. 2).

47. Reagents

47.1 *Sodium Hydroxide Coated Non-Fibrous Silicate*,

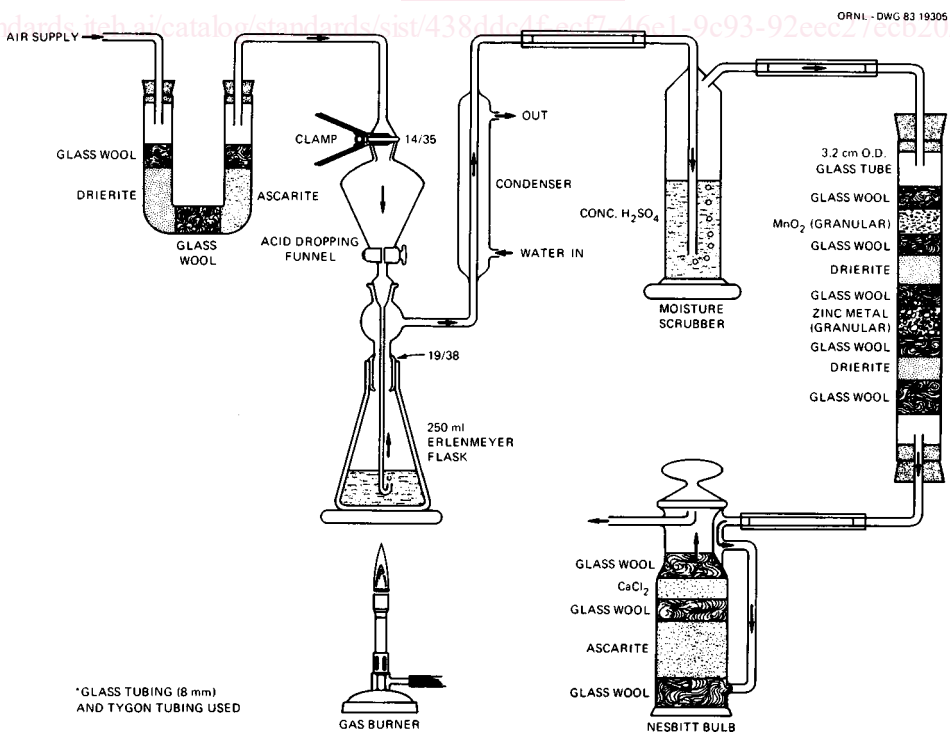


FIG. 2 Carbonate Apparatus

indicating (Ascarite II).[12]

47.2 *Anhydrous Calcium Sulfate*, indicating (Drierite).[12]

47.3 *Glass Wool*.

47.4 *Manganese Dioxide*, granular.

47.5 *Zinc Metal*, granular.

47.6 *Sulfuric Acid* (H_2SO_4, sp gr 1.84).

47.7 *Hydrochloric Acid* (5.5 *M*)—Dilute 50 mL of HCl (sp gr 1.19) to 100 mL with water.

48. Procedure

48.1 Weigh a sample (maximum of 5 g) to the nearest 0.01 g. The sample should contain approximately 20 mg CO_2. Transfer to an Erlenmeyer flask and add enough water to cover the inlet tube.

48.2 Attach the Nesbitt bulb, open the stopper and pass air through the apparatus for 10 to 15 min at the rate of 2 to 3 bubbles/s.

NOTE 17—Measure the flow rate at the H_2SO_4 moisture trap.

48.3 Remove the Nesbitt bulb without altering the air flow. Close the stopper and weigh the bulb to nearest 0.1 mg.

48.4 Open the stopper of the bulb and replace it on the apparatus.

48.5 Place 25 mL of 5.5 *M* HCl in the dropping funnel and force it into the flask by replacing the air inlet tube.

NOTE 18—If the uranium-ore concentrate was produced as a uranium peroxide, replace 25 mL of 5.5 *M* HCl with 25 mL of 5.5 *M* H_2SO_4 to prevent the release of chlorine.

48.6 Heat the Erlenmeyer flask with a small burner until the acid boils and adjust the burner to maintain gentle boiling.

48.7 Boil for 15 min, then shut off the flame.

48.8 Continue to pass air through the apparatus for an additional 10 min.

48.9 Remove the Nesbitt bulb and close the stopper immediately.

48.10 Reweigh the Nesbitt bulb to the nearest 0.1 mg.

48.11 Remove the Erlenmeyer flask from the apparatus while air is still flowing.

NOTE 19—Leave the air on until the flask is removed to prevent suck-back of the H_2SO_4.

48.12 Repeat the procedure in 48.1-48.10, without a sample, to obtain a blank.

49. Calculation

49.1 Calculate the percentage of carbonate, C_a, for the sample and the blank as follows:

$$C_a = \frac{136.36\,(B-C)}{A} \tag{10}$$

where:

A = sample weight, g,
B = weight of Nesbitt bulb after absorption of CO_2, g, and
C = weight of Nesbitt bulb before absorption of CO_2, g.

49.2 Correct the percentage of CO_3 obtained on the sample for a blank.

49.3 Calculate the weight percentage of carbonate, C_u, on a uranium basis as follows:

$$C_u = \frac{C_c \times 100}{U} \tag{11}$$

where:

C_c = corrected percentage of carbonate in the sample (see 49.2), and
U = uranium in the sample, %.

50. Pecision and Bias

50.1 *Precision*—A relative standard deviation for this test method has been reported at 5 % at 1.0 % carbonate level (see 4.2).

50.2 *Bias*—For information about the bias of this test method see 4.2.

FLUORIDE BY ION-SELECTIVE ELECTRODE

51. Scope

51.1 This test method covers the determination of fluoride in uranium-ore concentrates.

52. Summary of Test Method

52.1 The fluoride is separated pyrohydrolytically by passing a stream of moist oxygen over a mixture of sample and fluoride-free uranium oxide (U_3O_8) in a reactor tube at 850°C. (The U_3O_8 acts as an accelerator in the presence of high concentrations of sodium, calcium, or magnesium.) The HF formed is absorbed in a dilute solution of sodium hydroxide and the fluoride ion concentration is measured with an ion-selective electrode **(7, 8, 9).**

53. Interferences

53.1 At the specification limit for fluoride, interference effects are insignificant.

54. Apparatus

54.1 *Pyrohydrolysis Apparatus*, (see Fig. 3).

54.2 *Gas-Flow Regulator and Flowmeter*.

54.3 *Three-Necked 1-L Flask*.

54.4 *Gas Diffuser*.

54.5 *Thermometer*.

54.6 *Male Ball-Joint Connector*.

54.7 *Heating Mantle*, for 1-L flask, controlled by variable transformer.

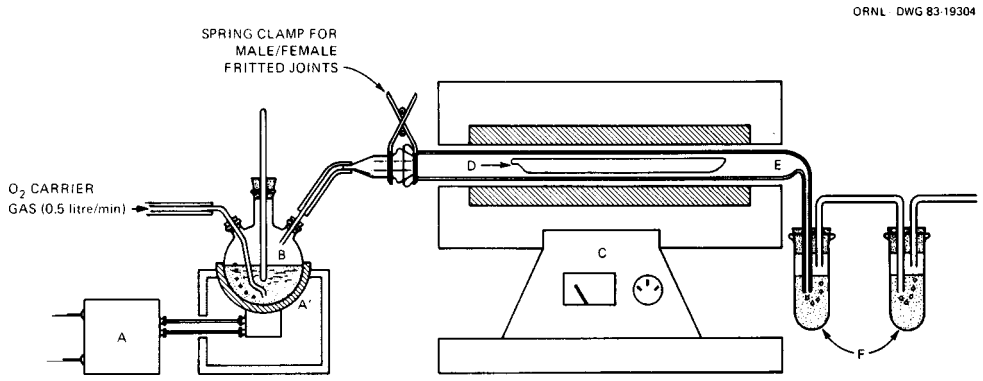
54.8 *Furnace*—A tube furnace capable of maintaining a temperature of 850°C. The bore of the furnace should be a minimum of 32 mm (1¼ in.) in diameter and 330 mm (13 in.) in length.

54.9 *Reactor Tube*, made from clear silica about 30 mm (1⅛in.) in diameter and 460 mm (18 in.) in length having a female ball-joint connector at the entrance end and a delivery tube 9.5 mm (⅜ in.) in diameter and 150 mm in length fused at right angles to the exit end.

54.10 *Absorption Vessels*—50-mL glass test tubes.

54.11 *Combustion Boat*—A quartz boat with 10-mL capacity and dimensions (100 mm long, 15 mm wide, and 10 mm deep.

[12] Ascarite II and Drierite have been found to be acceptable for this application. They are, respectively, the trademarks of Arthur H. Thomas and W. A. Hammond Drierite Companies.



A, A′—Heating jacket controlled by variable transformer. Nominal temperature 80 to 85°C for water.
B—One-liter three-necked with gas diffuser and thermometer 0 to 110°C. D.D. water used.
C—Tube furnace, controlled by variable transformer with thermocouple. Operating temperature 850 ± 25°C.
D—Sample boat.
E—Pyrohydrolytic tube.
F—Collection system; 10 mL of 0.2 *N* sodium hydroxide in first tube, 10 to 15 mL of water in second tube.

FIG. 3 Pyrohydrolysis Apparatus

54.12 *Fluoride-Ion Selective Electrode.*

54.13 *Millivolt Meter*, with saturated calomel reference electrode capable of reading to 1 mV.

54.14 *Magnetic Stirrer*.

55. Reagents

55.1 *Accelerator*—Fluoride-free uranium oxide (U_3O_8).

55.2 *Sodium Hydroxide Solution* (NaOH, 0.2 *N*)—Dissolve 8 g of NaOH in distilled water and dilute to 1 L.

55.3 *Buffer Solution* (0.001 *N*)—Dissolve 0.1 g of potassium acetate ($KC_2H_3O_2$) in water. Add 0.050 mL of acetic acid (sp gr 1.05) and dilute to 1 L.

55.4 *Fluoride Solution, Standard* (1 mL = 10 µg F)—Dissolve in water 0.221 g of sodium fluoride (NaF) previously dried at 110°C and dilute to 1 L in a volumetric flask. Pipet 10.0 mL of this solution into a 100-mL volumetric flask and dilute to volume with water. Mix and transfer the solution to a plastic container.

56. Procedure

56.1 Adjust the pyrohydrolysis system to operating conditions as follows:

56.1.1 Place the reactor tube in the furnace with the delivery tube as close as possible to the end (5 to 10 mm).

56.1.2 Turn on the furnace and allow it to reach 850°C. Adjust the controls to maintain this temperature within ±25 °C.

56.1.3 Fill the three-necked flask half full with water.

56.1.4 Place the flask on the heating mantle, then connect the gas diffuser to the flowmeter and the female socket to the reactor tube with a spring clamp.

56.1.5 Adjust the control on the heating mantle to bring the temperature of the water to 80 to 85°C.

56.1.6 Turn on the oxygen and adjust the flow to 500 mL/min. Flush the apparatus in this manner for 10 to 15 min.

56.2 Weigh 4 ± 0.01 g of powdered sample, mix thoroughly with 8 g of U_3O_8 accelerator, and place in a sample boat.

NOTE 20—A blank of 8 g U_3O_8 is run in a separate boat.

56.3 Connect the collection system. The collection system consists of two 50-mL test tubes in series. The first tube contains 10 mL of 0.2 *N* NaOH. The second tube contains 10 to 15 mL of water. The first tube is fitted with a two-holed stopper through which is passed the quartz delivery tube from the pyrohydrolysis apparatus and a glass inverted U-tube leading to the second tube. The gas stream escaping from the first tube during pyrohydrolysis is carried through the inverted U-tube into the water in the second test tube. Sufficient back pressure is created to ensure that all the fluoride is absorbed in the first tube.

NOTE 21—The delivery tube tip should be immersed to a depth of 15 mm below the surface of the NaOH solution.

56.4 Position the sample boat in the middle of the reactor tube and immediately close the tube.

56.5 Pyrohydrolyze for 60 min.

56.6 Remove the first test tube containing NaOH solution and rinse the delivery tube with distilled water into the tube.

56.7 Transfer the contents of the test tube to a 25-mL volumetric flask. Dilute to mark and mix.

56.8 Pipet 1 mL into a 100-mL plastic beaker, add 24 mL of water and 25 mL of buffer solution.

56.9 Place in a magnetic stirrer and insert the electrode pair.

56.10 Set the meter at the millivolt setting and stir the sample solution until a stable reading is reached. Record the millivolt reading.

56.11 Rinse electrodes with water and dry with absorbent tissue.

56.12 Read all samples and blank.

56.13 Prepare a calibration curve by adding, to separate 100-mL plastic beakers, the following amounts of fluoride standard solution (1 mL = 10 µg of fluoride): 0, 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mL. Dilute to 25 mL with distilled water. Add 25 mL of buffer solution just prior to measuring each standard individually as in 56.15 and 56.16. Plot mV readings against micrograms of fluoride using log/linear graph paper.

57. Calculation

57.1 Calculate the percentage of fluoride, *F*, as follows:

$$F = \frac{(C_s - C_B)}{W \times 400} \quad (12)$$