



Designation: C1022 – 05

Standard Test Methods for Chemical and Atomic Absorption Analysis of Uranium-Ore Concentrate¹

This standard is issued under the fixed designation C1022; 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 C967.

1.2 The analytical procedures appear in the following order:

	Sections
Uranium by Ferrous Sulfate Reduction—Potassium Dichromate Titrimetry	9
Nitric Acid-Insoluble Uranium	10 to 18
Extractable Organic Material	19 to 26
Determination of Arsenic	27
Carbonate by CO ₂ Gravimetry	28 to 34
Fluoride by Ion-Selective Electrode	35 to 42
Halides by Volhard Titration	43 to 50
Moisture by Loss of Weight at 110°C	51 to 57
Phosphorus by Spectrophotometry	58 to 66
Determination of Silicon	67
Determination of Thorium	68
Calcium, Iron, Magnesium, Molybdenum, Titanium, and Vanadium by Atomic Absorption Spectrophotometry	69 to 78
Potassium and Sodium by Atomic Absorption Spectrophotometry	79 to 88
Boron by Spectrophotometry	89 to 98

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. A specific precautionary statement is given in Section 7.*

2. Referenced Documents

2.1 ASTM Standards:²

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

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride
- C859 Terminology Relating to Nuclear Materials
- C967 Specification for Uranium Ore Concentrate
- C1110 Practice for Sample Preparation for X-Ray Emission Spectrometric Analysis of Uranium in Ores Using the Glass Fusion or Pressed Powder Method
- C1219 Test Methods for Arsenic in Uranium Hexafluoride
- C1254 Test Method for Determination of Uranium in Mineral Acids by X-Ray Fluorescence
- C1267 Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium
- C1287 Test Method for Determination of Impurities in Nuclear Grade Uranium Compounds by Inductively Coupled Plasma Mass Spectrometry
- C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
- D1193 Specification for Reagent Water
- E60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology C859.

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 C967.

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.³ Other grades may be used, provided it is first ascertained that the reagent is of 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 D1193.

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 C967.

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. This test method was discontinued in January 2002 and replaced with Test Method C1267.

9.2 The uranium content of the sample may also be determined using Test Method C1254. The user's laboratory must establish and document method performance.

NOTE 1—Dissolution of UOC samples may be achieved using the techniques or combination of techniques described in C1347. The laboratory must validate the performance of C1347 using characterized UOC samples. If C1347 methods are not suitable for UOC sample dissolution, the user may establish and document applicable dissolution methods.

³ *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.

NITRIC ACID-INSOLUBLE URANIUM

10. Scope

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

11. Summary of Test Method

11.1 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.

12. Interference

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

13. Apparatus

13.1 *Digestion Flask*, 500-mL, with side entry tube and attached reservoir.

13.2 *Stirring Apparatus*, with sleeve-type stirrer.

13.3 *Heating Mantle*, 250-W, controlled by a variable transformer.

13.4 *Büchner Funnel*.

13.5 *Porcelain Crucibles*, 40-mL.

13.6 *Muffle Furnace*.

13.7 *Filter Paper*,⁴ of medium porosity.

13.8 *Spectrophotometer*, with 1-cm cells that are in accordance with Practice E60.

14. Reagents

14.1 *Nitric Acid (10 M)*—Dilute 62.5 mL of HNO₃ (sp gr 1.42) to 100 mL with distilled water.

14.2 *Nitric Acid (1 M)*—Dilute 62.5 mL of HNO₃ (sp gr 1.42) to 1 L with distilled water.

14.3 *Sodium Hydroxide (100 g/L)*—Dissolve 10 g of NaOH in 100 mL of water.

14.4 *Hydrogen Peroxide (H₂O₂, 30 %)*.

14.5 *Hydrochloric Acid (HCl, sp gr 1.19)*.

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

14.7 *Sulfuric Acid (9 M)*—Add 500 mL H₂SO₄ (sp gr 1.84) to 500 mL of iced water with constant stirring. Cool and dilute to 1 L with water.

15. Procedure

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

15.2 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.

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

⁴ Whatman brand No. 40 or its equivalent has been found suitable.

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

NOTE 2—The stirrer is started before the acid is added to prevent material from sticking to the flask.

15.5 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.

15.6 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.)

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

15.8 Remove the thermometer and carefully rinse with water all slurry that adheres to it.

15.9 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.

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

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

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

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

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

15.15 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 H₂O₂ (30 %) have been added as a color developer.

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

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

15.18 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.

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

15.20 Cool the crucible in a desiccator and weigh.

15.21 Calculate the percentage of solids in accordance with 17.1.

NOTE 3—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 16.1-16.10.

16. Photometric Procedure for Uranium

16.1 Transfer the ground, blended residue from 15.20 to a 100-mL beaker.

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

16.3 Add 5 mL of HNO₃ (sp gr 1.42) and boil until fuming of NO₂ ceases. Remove cover glass.

16.4 Add 5 mL of 9M H₂SO₄ and 2 mL of HF (48 %), then heat to dryness on the hotplate. Bake to fume off remaining H₂SO₄ and cool.

16.5 Wash down sides of beaker with water and add 5 mL of HNO₃.

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

16.7 Quantitatively transfer the solution to a 250-mL volumetric flask. Add 25 mL of NaOH solution and a few drops of H₂O₂. Make up to mark with water and mix.

NOTE 4—The solution must be basic for yellow sodium peruranate color to develop.

16.8 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 H₂O₂, to 250 mL with water.

16.9 Prepare a calibration curve covering the range from 0 to 50 mg of uranium from aliquots of a standard uranium solution. Proceed as in 16.5-16.8. Plot the milligrams of uranium against absorbance readings.

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

NOTE 5—If the sample solution falls outside the calibration range, dilute a portion with the reference-blank solution and read again.

17. Calculation

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

$$R = \frac{R_w \times 100}{S_w} \quad (1)$$

where:

R_w = weight of residue (see 15.20), g, and

S_w = weight of samples, g.

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

$$U_N = \frac{U}{S_w \times 10} \quad (2)$$

where:

U = uranium content calculated in 16.10, mg, and

S_w = weight of sample, g.

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

$$U_u = \frac{U_N \times 100}{U_s} \quad (3)$$

where:

U_N = nitric acid-insoluble residue present (see 17.2), %, and

U_s = uranium in sample, %.

18. Precision and Bias

18.1 *Precision*—A relative standard deviation for this test method has been reported as 10 % at the 0.2 % HNO₃ insoluble uranium level (see 4.2).

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

EXTRACTABLE ORGANIC MATERIAL

19. Scope

19.1 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.

20. Summary of Test Method

20.1 This test method consists of a dual extraction using *n*-hexane 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.

21. Interferences

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

22. Apparatus

22.1 *Soxhlet Extraction Apparatus*—The *n*-hexane extraction is done in a Soxhlet extraction apparatus. Construct as follows (see Fig. 1):

22.1.1 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.

22.1.2 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. A 250-mL heating mantle connected to a 7.5-A variable transformer shall be used to heat this.

22.1.3 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.

22.1.4 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 *n*-hexane is used for the extraction.

22.2 *Heat gun* (hot-air electric dryer), may be used to evaporate the solvent in procedure 24.6 or 24.15.

22.3 *Extraction Thimbles*.

22.4 *Filter Paper*.⁵

22.5 *Phase Separator Paper*.⁶

23. Reagents

23.1 *n*-hexane—Whenever a new supply is used, it should be checked for nonvolatile residue. Evaporate 100.0 mL just to

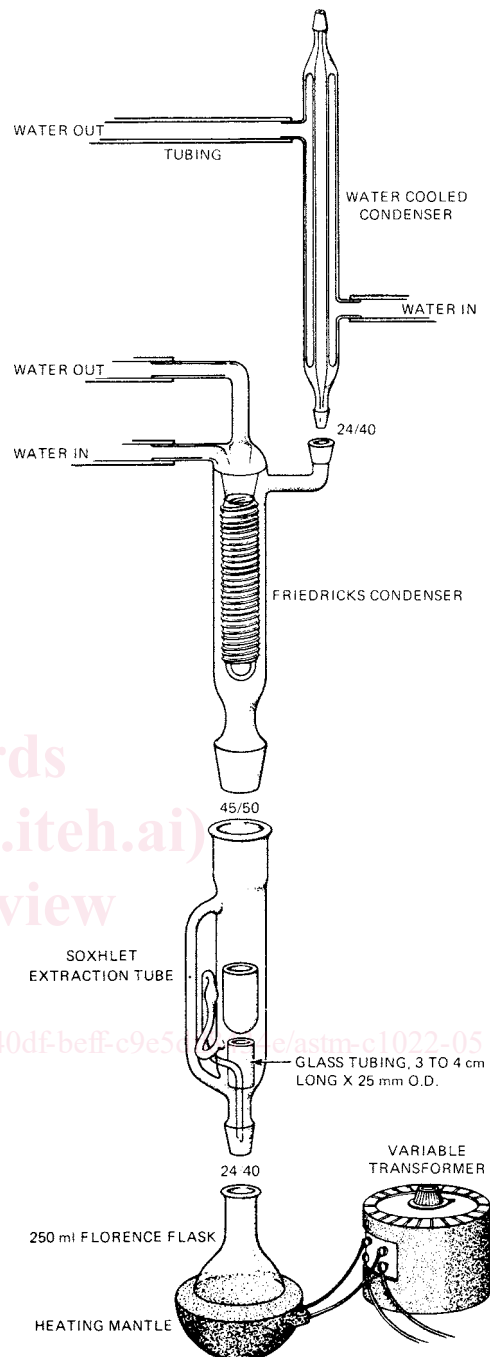


FIG. 1 Hexane Extraction Unit

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.

23.2 *Nitric Acid (1 + 1)*—Mix equal volumes of concentrated (sp gr 1.42) reagent grade HNO₃ and distilled water.

23.3 *Chloroform*—Whenever a new supply of chloroform is to be used, it should be checked for nonvolatile residue as described in 23.1.

⁵ Whatman brand size 33 by 94 mm has been found suitable.

⁶ Whatman IPS has been found suitable.

24. Procedure

24.1 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.

24.2 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.

24.3 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 6—Tap water may be used in cooling both condensers if the amount of reagent lost during the refluxing (see 24.5) is not greater than 10 % of the volume added in 24.4. 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.

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

24.5 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.

24.6 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 7—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.

24.7 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 8—Do not allow the temperature of the dish to go below the dewpoint.

24.8 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 9—This weight is in grams as W_2 .

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

24.10 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.

24.11 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.

24.12 Allow the phases to separate.

NOTE 10—If emulsions form, transfer to centrifuge tubes and centrifuge to separate the phases.

24.13 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.

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

24.15 Place the platinum dish in a hood and evaporate until about 1 mL of chloroform remains. This evaporation may be done as described in 24.6.

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

24.17 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 11—This weight is in grams as W_3 .

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

NOTE 12—This weight is in grams as W_4 .

25. Calculation

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

$$O_m = \frac{100 [(W_2 - W_1) + 2 (W_3 - W_4)]}{S_w} \quad (4)$$

where:

W_2 = weight of platinum dish in 24.8, g,

W_1 = weight of platinum dish in 24.6, g,

W_3 = weight of platinum dish in 24.17, g,

W_4 = weight of platinum dish in 24.18, g, and

S_w = weight of sample.

26. Precision and Bias

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

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

DETERMINATION OF ARSENIC

27. Scope

27.1 The determination of Arsenic by diethyldithiocarbamate photometric method has been discontinued. Interested persons can obtain a copy in the C1022-02 version.

27.2 With appropriate sample preparation, Atomic Absorption Spectrometry as described in Test Methods C1219 may be used for arsenic determination.

27.3 As an alternative and with appropriate sample preparation, ICP-MS as described in Test Method C1287 may be used for arsenic determination.

CARBONATE BY CO₂ GRAVIMETRY

28. Scope

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

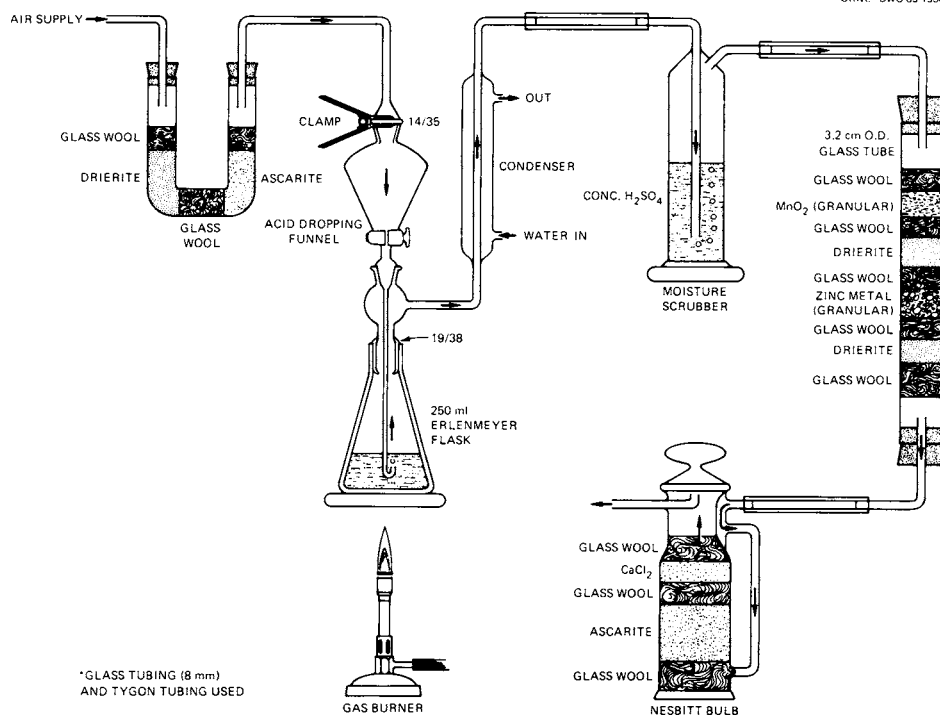


FIG. 2 Carbonate Apparatus

*GLASS TUBING (8 mm) AND TYGON TUBING USED

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

29. Summary of Test Method

29.1 The carbonate in the sample is decomposed with hydrochloric acid and evolved as carbon dioxide. The incoming air is dried and the CO₂ is removed by passing it through NaOH and anhydrous calcium sulfate (CaSO₄). The evolved gases are scrubbed in H₂SO₄ to remove moisture and passed through a tower of manganese dioxide and zinc metal to remove any SO₂ or H₂S formed. The evolved gas is then absorbed by NaOH in a Nesbitt bulb and determined gravimetrically (1).

30. Apparatus

30.1 Carbonate Apparatus, (see Fig. 2).

31. Reagents

31.1 Sodium Hydroxide Coated Non-Fibrous Silicate, indicating (Ascarite II).⁷

31.2 Anhydrous Calcium Sulfate, indicating (Drierite).⁷

31.3 Glass Wool.

31.4 Manganese Dioxide, granular.

31.5 Zinc Metal, granular.

31.6 Sulfuric Acid (H₂SO₄, sp gr 1.84).

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

⁷ 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.

32. Procedure

32.1 Weigh a sample (maximum of 5 g) to the nearest 0.01 g. The sample should contain approximately 20 mg CO₂. Transfer to an Erlenmeyer flask and add enough water to cover the inlet tube.

32.2 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 13—Measure the flow rate at the H₂SO₄ moisture trap.

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

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

32.5 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 14—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 H₂SO₄ to prevent the release of chlorine.

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

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

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

32.9 Remove the Nesbitt bulb and close the stopper immediately.

32.10 Reweigh the Nesbitt bulb to the nearest 0.1 mg.

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

NOTE 15—Leave the air on until the flask is removed to prevent suck-back of the H₂SO₄.