Designation: E 1506 – 97

Standard Test Methods for Analysis of Acid-Grade Calcium Fluoride (Fluorspar)[1]

This standard is issued under the fixed designation E 1506; 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 the chemical analyses of acid-grade calcium fluoride (fluorspar). These test methods appear in the following sections:

	Sections
Volatiles as Moisture	6-13
Silica	14-22
Assay as Calcium Fluoride (CaF_2)	23-32
Soluble Chloride as NaC1	33-50
Calcium Carbonate	51-59
Phosphorus	60-69
Arsenic	70-78
Mixed Oxides (R_2O_3)	79-87
Sulfide Sulfur	88-96

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.*

1.4 Review the current Material Safety Data Sheet (MSDS) for each chemical used in this standard for detailed information concerning toxicity, first-aid procedures, handling, and safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

E 300 Practice for Sampling Industrial Chemicals[3]

3. Significance and Use

3.1 Calcium fluoride is available in nature in various forms and purities. A major use for it is in the manufacture of hydrofluoric acid. The test methods listed in 1.1 provide procedures for analyzing calcium fluoride to determine whether it is suitable for this use.

4. Reagents

4.1 *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.[4] 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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

5. Sampling

5.1 Sampling of calcium fluoride is not within the scope of these test methods. See the appropriate sections of Practice E 300 for sampling procedures.

VOLATILES AS MOISTURE

6. Scope

6.1 This test method covers the determination of volatiles as percent moisture.

7. Summary of Test Method

7.1 The sample is dried in an air oven at 105 to 110°C, and the weight loss is calculated as percent moisture.

8. Apparatus

8.1 *Top-Loading Balance*, capable of weighing 1000 g to the nearest 0.01 g.

8.2 *Sample Pan*, stainless steel or borosilicate glass, 152 by 152 by 51 mm (6 by 6 by 2 in.) deep.

8.3 *Cooling Rack*, wood or metal, able to allow circulation of air around the entire sample pan (for example, a “baker’s rack”).

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[1] These test methods are under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and are the direct responsibility of Subcommittee E15.59 on Acid Grade Fluorspar.

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

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.4 *Forced Air Oven*, capable of maintaining temperatures of 105 to 110°C.

9. Hazards

9.1 See 1.3 and 1.4.

10. Procedure

10.1 Tare a clean, dry sample pan to the nearest 0.01 g.

10.2 Add approximately 1000 g of representative sample to the pan and spread evenly. Wipe all external surfaces of the pan free of sample. Weigh again to the nearest 0.01 g.

10.3 Place the pan containing the sample in an air oven at 105 to 110°C for a minimum of 12 h.

10.4 Remove the pan from the oven and place on a cooling rack for 1 h.

10.5 Weigh the cooled pan to the nearest 0.01 g.

10.6 Return the pan to the cooling rack and cool for an additional 30 min. Then reweigh the pan to the nearest 0.01 g.

10.7 Repeat 11.6 until consecutive weights agree within 0.05 g.

10.8 Once a consistent weight has been obtained, dump the sample on a flat, dry surface and spread it with a spatula. If the fluorspar is dry, it will appear dusty, powdery, and flour-like in consistency. If the fluorspar does not appear as such, repeat the analysis using fresh sample.

11. Calculation

11.1 Calculate percent volatiles as moisture as follows:

$$\text{volatiles as moisture, weight \%} = \frac{(B - C) \times 100}{(B - A)} \quad (1)$$

where:

A = weight of empty pan, g (10.1),
B = weight of pan plus sample before drying, g (10.2), and
C = weight of pan plus sample after drying to consistent weight, g (10.7).

12. Report

12.1 Report the percent volatiles as moisture to the nearest 0.01 %.

13. Precision and Bias

13.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 1):

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value shown in Table 1.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be the value shown in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value shown in Table 2.

TABLE 1 Volatiles as Moisture Checking Limits for Duplicates

Volatiles Level, %	Standard Deviation	Degrees of Freedom	95 % Limit, % Absolute
6	0.0257	18	0.072
9	0.0822	18	0.230

TABLE 2 Volatiles as Moisture

Volatiles Level,%	Repeatability			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit, % Absolute	Standard Deviation	Degrees of Freedom	95 % Limit,% Absolute
6	0.0238	9	0.067	0.0807	8	0.226
9	0.0666	9	0.186	0.0865	8	0.242

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be the value shown in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value shown in Table 2.

NOTE 1—These precision estimates are based on an interlaboratory study performed in 1992 in which samples of fluorspar from two lots, one containing about 6 % volatiles as moisture and the other about 9 % volatiles as moisture, were each analyzed in duplicate by one analyst on each of two days in each of ten laboratories for a total of 120 determinations.[5] Practice E 180 was used in developing these precision estimates.

13.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

SILICA

14. Scope

14.1 This test method covers the determination of percent silica.

15. Summary of Test Method

15.1 The sample is treated with 10 % acetic acid to remove carbonates and soluble salts, the residue is ignited in a 650°C muffle furnace, treated with 48 % hydrofluoric acid (HF), and then heated again at 650°C. The weight loss after the HF treatment is calculated as percent silica.

16. Apparatus

16.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

16.2 *Beaker*, 150-mL glass, unscratched, and watchglass cover.

16.3 *Graduated Cylinder*, 25-mL glass.

16.4 *Graduated Cylinder*, 10-mL polypropylene.

16.5 *Platinum Crucible*, 30-mL capacity with lid.

16.6 *Platinum Wire*, 4 cm by 2 mm.

16.7 *Stirring Rod*, borosilicate glass, unscratched.

16.8 *Muffle Furnace*, capable of maintaining a temperature of 650 ± 10°C or higher.

16.9 *Desiccator*, with desiccant.

16.10 *Steam Bath*.

16.11 *Glass Filter Funnel*.

16.12 *Bunsen Burner*, ringstand, ring, and heating mesh.

[5] Supporting data are available from ASTM Headquarters. Request RR: E15-1027.

16.13 *Disposable Pipets*.

16.14 *Mortar and Pestle*, 102-mm (4-in.) diameter, agate.

16.15 *Tongs*, platinum-tipped.

17. Reagents

17.1 *Acetic Acid Solution* (100 mL/L)—Dilute 10 mL of glacial acetic acid to 100 mL with water; mix well.

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

17.3 *Ashless Cellulose Filter Aid*, Whatman accelerator powder,[6] or equivalent.

17.4 *Filter Paper*, 9-cm diameter, low-ash, acid-washed, medium-porosity, able to retain 8-µm particles.

17.5 *Filter Paper*, 9-cm diameter, low-ash, acid-washed, fine-porosity, able to retain 2.5-µm particles.

17.6 *Ethanol*, pure or denatured.

17.7 *Filter Pulp Slurry* (40 g/L)—Slurry 10 g of cellulose filter aid with 250 mL of water.

18. Hazards

18.1 See 1.3 and 1.4.

19. Procedure

19.1 Transfer 8 to 10 g of sample (previously dried to constant weight at 105 to 110°C) into a mortar. Grind with a pestle until the particle size is 100 to 500 mesh.

19.2 Weigh 1.0 g of the ground sample to the nearest 0.0001 g, and transfer it to a 150-mL beaker.

19.3 Wet the sample with 1 mL of ethanol, then add 15 mL of 10 % acetic acid to the beaker.

19.4 Add a glass stirring rod to the beaker, cover with a watchglass, and place on a steam bath.

19.5 Heat for 30 ± 1 min, stirring every 5 min.

19.6 Remove from the steam bath, add 5 mL of filter pulp slurry to the beaker, cover, and allow to sit for approximately 12 h.

19.7 Gravity filter the solution through medium-porosity filter paper.

19.8 Rinse the beaker several times with minimal portions of hot water (total wash water approximately 35 mL), filtering each wash through the same filter paper. Save the filtrate for the determination of Mixed Oxides (Section 79).

19.9 Wipe the beaker clean with one fourth of a fine-porosity filter paper, and transfer the wipe paper and the filter paper with the residue into a 30-mL platinum crucible.

19.10 Place a platinum wire across the top of the platinum crucible. Rest the crucible lid on the wire and place the crucible into a cool muffle furnace.

19.11 Heat the furnace slowly (1-h cycle) to 650 ± 10°C. Once the temperature has reached 650°C, check the crucible every 10 min until the paper is entirely burned off.

19.12 Cool the crucible to room temperature in a desiccator, then weigh the crucible, cover, and residue to 0.0001 g.

19.13 Using a 10-mL polypropylene graduate cylinder, carefully pour 3 mL of 48 % HF into the crucible.

19.14 Gently heat the crucible over a Bunsen burner in a hood until dry (see Note 2).

NOTE 2—The solution must be heated below boiling. Excess heat will cause erratic results. If unable to control heating using a bunsen burner, heat the solution on a hot plate at 60°C or below. Evaporation of the 6 mL of HF used in this procedure should take approximately 2 h.

19.15 Cool the crucible, then repeat 19.13 and 19.14.

19.16 Cover the crucible with a platinum lid; then carefully place it into a muffle furnace maintained at 650 ± 10°C.

19.17 Heat the crucible for 5 min; then place it into a desiccator to cool.

19.18 Weigh the crucible, cover, and residue to 0.0001 g.

20. Calculation

20.1 Calculate percent silica as follows:

$$\text{silica, weight \%} = \frac{(B - C) \times 100}{A} \quad (2)$$

where:

A = weight of sample, g (19.2),

B = weight of crucible, cover, and residue before HF treatment, g (19.12), and

C = weight of crucible, cover, and residue after HF treatment, g (19.18).

21. Report

21.1 Report the percent silica to the nearest 0.01 %.

22. Precision and Bias

22.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 3):

22.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0319 % absolute at 50 df. The 95 % limit for the difference between two such runs is 0.09 % absolute.

22.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be 0.0362 % absolute at 25 df. The 95 % limit for the difference between two such averages is 0.10 % absolute.

22.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.0529 % absolute at 11 df. The 95 % limit for the difference between two such averages is 0.15 % absolute.

NOTE 3—These precision estimates are based on an interlaboratory study performed in 1992 in which samples of fluorspar from two lots, one containing about 0.5 % silica and the other about 1 % silica, were each analyzed in duplicate on each of two days by one analyst in each of 14 laboratories for a total of 112 determinations.[5] Practice E 180 was used in developing these precision estimates.

22.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

ASSAY AS CALCIUM FLUORIDE (CaF_2)

23. Scope

23.1 This test method covers the determination of assay as percent calcium fluoride (CaF_2).

[6] Available from Whatman LabSales, P.O. Box 1359, Hillsboro, OR, 97123-9981.

24. Summary of Test Method

24.1 The residue remaining after the determination of silica (see 19.18) is treated with H_2SO_4, dried, then dissolved in HCl. Ammonium oxalate is added to the HCl solution to precipitate calcium oxalate, then the precipitate is dried and weighed. Percent CaF_2 is calculated from the weight of the calcium oxalate collected.

25. Interferences

25.1 Iron causes a positive interference. If iron is suspected to be present, its effect can be minimized by adding 1 mL of concentrated HNO_3 to the solution described in 29.8 before boiling.

25.2 Strontium precipitates, as the oxalate, along with calcium oxalate to produce erroneously high results.

25.3 A small amount of CaF_2 is lost in the acetic acid treatment used in 19.3, resulting in an erroneously low result. To correct for this loss, the term 0.15 is included in the calculation in 30.1.

26. Apparatus

26.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

26.2 *Beakers*, borosilicate glass, 800-mL, 400-mL, and watchglass covers.

26.3 *Graduated Cylinders*, borosilicate glass, 10-mL, 25-mL.

26.4 *Platinum Crucible*, 30-mL capacity with lid.

26.5 *Platinum Wire*, 4 cm by 2 mm.

26.6 *Stirring Rod*, borosilicate glass.

26.7 *Muffle Furnace*, capable of maintaining a temperature of 1200 ± 10°C or higher.

26.8 *Desiccator*, with desiccant.

26.9 *Funnel*, borosilicate glass.

26.10 *Bunsen Burner*.

26.11 *Ringstand*, equipped with ring and heating gauze.

26.12 *Tongs*, platinum- or nickel-tipped.

27. Reagents

27.1 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

27.2 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

27.3 *Hydrochloric Acid Solution* (1 + 1)—Wearing goggles, carefully add 250 mL of concentrated HCl (sp gr 1.19) to 250 mL of water. Mix well.

27.4 *Ammonium Chloride* (NH_4Cl).

27.5 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

27.6 *Ammonium Oxalate Solution (Saturated)*—Add 30 g of ammonium oxalate to a 1-L polyethylene bottle. Add 1000 mL of hot water to the bottle and mix well. Allow the solution to cool. Add additional ammonium oxalate if necessary to keep crystals present at the bottom of the bottle at all times.

27.7 *Ammonium Oxalate Solution* (1 g/L)—Add 0.1 g of ammonium oxalate to 100 mL of water and mix well.

27.8 *Filter Paper*, 9-cm diameter, low-ash, acid-washed, medium-porosity, able to retain 8-µm particles.

27.9 *Filter Pulp Slurry* (40 g/L)—Slurry 10 g of cellulose filter aid with 250 mL of water.

27.10 *pH Paper*—Litmus.

28. Hazards

28.1 See 1.3 and 1.4.

29. Procedure

29.1 Add 5 mL of concentrated sulfuric acid to the residue remaining in the crucible from 19.18.

29.2 Partially cover the crucible and gently heat over a bunsen burner in a hood until all H_2SO_4 is driven off (see Note 4).

NOTE 4—Do not heat directly with the flame.

29.3 Repeat 29.1 and 29.2 using 3 mL of concentrated sulfuric acid.

29.4 Cool the crucible and transfer the crucible, cover, and residue into a 400-mL beaker.

29.5 Add 10 mL of concentrated hydrochloric acid, 5 g of ammonium chloride, and 200 mL of hot water to the beaker; mix well.

29.6 Warm the solution to between 70 and 80°C on a hot plate in a hood; keep at this temperature for 2 h.

29.7 Remove the crucible and lid from the solution using platinum or nickel-tipped tongs. Rinse each with warm water, collecting the washings in the beaker. Scrape any remaining residue from the crucible into the solution with a rubber policeman.

29.8 Cover with a watchglass, then boil the solution for 10 min to dissolve any solid matter (see Note 5 and 25.1).

NOTE 5—If insolubles are still present after the 10-min boil, filter the solution through medium-porosity filter paper, then return the residue and paper to the crucible. Place platinum wire across the top of the crucible, rest the lid on the wire, and place the crucible into a cool muffle furnace. Heat the furnace slowly to 650°C (±10°C, 1-h cycle). At 650°C, check the crucible every 10 min until the paper burns off. Repeat 29.1 to 29.8 using 1 mL of concentrated sulfuric acid. Combine the filtrates in one beaker, then continue with 29.9.

29.9 Allow the solution to cool, then add ammonium hydroxide dropwise while mixing, until the solution tests basic (blue) to Litmus paper.

29.10 Mix well, cover, and then boil for 1 min.

29.11 Allow the solution to cool slightly. If necessary, add ammonium hydroxide dropwise while mixing until the solution tests basic (blue) to Litmus paper.

29.12 Gravity filter this solution through medium-porosity filter paper, into an 800-mL beaker.

29.13 Wash the filter paper and residue several times with hot water, collecting the filtrates in the 800-mL beaker (see 29.12).

29.14 Wash the filter paper and residue with 20 mL of hot 1 + 1 HCl solution, then four 20-mL portions of hot distilled water, collecting the filtrates in the 400-mL beaker.

29.15 Adjust the pH of the solution in the 400-mL beaker with ammonium hydroxide until it tests basic (blue) to Litmus paper.

29.16 Boil this solution for 1 min, then allow to cool slightly just below boiling.

29.17 Filter through the original filter paper. Wash with hot water and collect the filtrate in the 800-mL beaker. Save the

filter cake for the determination of Mixed Oxides (Section 79). Bring the filtrate to a boil. Add 100 mL of saturated ammonium oxalate solution, then add 5 mL of filter pulp slurry and stir to mix.

29.18 Boil the solution for 30 s, then allow it to cool until precipitate settles. The sample can sit overnight before filtering, if necessary or convenient.

29.19 Gravity filter the solution through medium-porosity filter paper.

29.20 Rinse the beaker with 10 to 15 mL of cold 0.1 % ammonium oxalate solution. Transfer the washings into the filter, using them to wash the precipitate.

29.21 Repeat 29.20 two more times.

29.22 Wash the residue with three 10 to 15-mL portions of 0.1 % ammonium oxalate solution.

29.23 Wash the residue with three 10 to 15-mL portions of cold water.

29.24 Weigh a 30-mL platinum crucible and cover to 0.0001 g (Weight *B*).

29.25 Transfer the filter paper and residue into the platinum crucible.

29.26 Place a platinum wire across the top of the platinum crucible, rest the lid on the wire, and place the crucible into a cool muffle furnace.

29.27 Heat the furnace slowly to 1200°C. Check to see if all paper is burned off.

29.28 Keep crucible at 1200°C for 20 min.

29.29 Remove crucible and place in a desiccator containing fresh desiccant; allow to cool to room temperature.

29.30 Immediately weigh the crucible, cover, and residue to 0.0001 g (Weight *C*).

30. Calculation

30.1 Calculate assay as percent CaF_2 as follows:

$$\text{assay as } CaF_2\text{, weight \%} = \frac{(C - B) \times 1.3923 \times 100}{A} + 0.15 \quad (3)$$

where:

A	=	weight of fluorspar sample, g, (see 19.2),
B	=	weight of crucible and cover, g, (see 29.24),
C	=	weight of crucible, cover, and residue, g (see 29.30),
1.3923	=	conversion factor for CaO (molecular weight (MW) = 56.08) to CaF_2(MW = 78.08), and
0.15	=	correction for amount of calcium fluoride lost in the acetic acid treatment, considered to be 0.0015 g CaF_2/g sample.

31. Report

31.1 Report the percent calcium fluoride to the nearest 0.01 %.

32. Precision and Bias

32.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 6):

32.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.1778 % absolute at 30 df. The 95 % limit for the difference between two such runs is 0.50 % absolute.

32.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be 0.1169 % absolute at 15 df. The 95 % limit for the difference between two such averages is 0.33 % absolute.

32.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.3559 % absolute at 6 df. The 95 % limit for the difference between two such averages is 1.00 % absolute.

NOTE 6—These precision estimates are based on an interlaboratory study performed in 1992 on two samples (one a commercial sample, the other a reference material) each containing approximately 98 % calcium fluoride. One analyst in each of eight laboratories performed duplicate determination of a sample of NIST Standard Reference Material 79a on each of two separate days for a total of 32 determinations. The same protocol was used on a sample of commercial material except that seven laboratories participated for a total of 28 determinations.[5] Practice E 180 was used in developing precision estimates.

32.2 *Bias*—An average of 97.71 % calcium fluoride was obtained on NIST Standard Reference Material 79a which has a certified value of 97.39 %. This certified value, with a standard deviation of 0.06 % absolute for a single determination, was obtained using the U.S. Customs Laboratory Method (volumetric permanganate) as given in the certificate.

SOLUBLE CHLORIDE AS NaCl

33. Volumetric Procedure, Scope

33.1 This test method covers the volumetric determination of trace quantities of soluble chloride as percent NaCl.

34. Summary of Test Method

34.1 Soluble chloride is extracted from fluorspar with hot water; the extract is filtered, then titrated to a colorimetric end point with standardized silver nitrate solution.

35. Apparatus

35.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

35.2 *Pipets*, 1-mL, 10-mL glass.

35.3 *Graduated Cylinder*, 100-mL glass.

35.4 *Beakers*, 150-mL, 250-mL.

35.5 *Burets*, 10-mL, 25-mL glass.

35.6 *Volumetric Flask*, 1-L glass.

36. Reagents

36.1 *Potassium Chromate Indicator Solution* (50 g/L)—Dissolve 50 g K_2CrO_4 in 500 mL of water. Add silver nitrate solution (see 36.3) until a definite red precipitate is formed. Allow to stand 12 h, filter through fine-porosity filter paper and dilute the filtrate to 1 L with water.

36.2 *Sodium Chloride Standard Solution* (0.0141 *N*)—Dissolve 0.8241 g of NaCl (previously dried to constant weight at 105 to 110°C) in water and dilute to 1 L; mix well.

36.3 *Silver Nitrate Standard Titrant* (0.0141 *N*)—Dissolve 2.395 g of $AgNO_3$(previously dried to constant weight at 105 to 110°C) in water and dilute to 1 L; mix well.

36.3.1 Pipet 10.0 mL of 0.0141 *N* NaCl (see 36.2) into a 150-mL beaker, add 40 mL of water and 1 mL of K_2CrO_4 indicator solution. Using a 25-mL buret, titrate this solution with the 0.0141 *N* $AgNO_3$ to a faint brown end point (see Note 7). Similarly determine a blank using all of the above reagents, but no NaCl. The titer of the $AgNO_3$ in µg Cl/mL, *A*, is as follows:

$$A = \frac{(500 \times 10)}{B} \quad (4)$$

where:
500 = Cl in 0.0141 *N* NaCl, µg/mL, and
B = $AgNO_3$ required for titration of the solution, net mL.

Store standardized solution in a brown glass bottle.

36.4 *Filter Paper*, 12.5-cm diameter, fine-porosity.

36.5 *Denatured Alcohol*.

37. Hazards

37.1 See 1.3 and 1.4.

38. Procedure

38.1 Weigh 25 g of sample (previously dried to constant weight at 105 to 110°C) to the nearest 1 g into a 150-mL beaker; wet the sample with 10 mL of denatured alcohol.

38.2 Add 100 mL of hot distilled water to the beaker. Using a magnetic stirrer, stir the mixture for 1 h; allow the mixture to cool and the fluorspar to settle.

38.3 After a minimum of 2-h settling time, gravity-filter the solution through a 12.5-cm diameter fine-porosity filter paper, collecting the filtrate in a 250-mL beaker.

38.4 Pipet 1 mL of potassium chromate indicator solution into the beaker.

38.5 Using a 10-mL buret, titrate with 0.0141 *N* $AgNO_3$ dropwise to a faint brown end point; mL = *A* (see Note 7).

NOTE 7—To aid in the determination of the end point, place a 250-mL beaker with the same volume of water and indicator next to the sample, as a comparator. The first brownish color that appears in the sample is the end point.

38.6 Similarly, determine a blank using all of the above reagents, but no sample; mL = *B*.

39. Calculation

39.1 Calculate percent soluble chloride as NaCl as follows:

$$\text{Soluble chloride as NaCl, weight \%} = \frac{(A - B) \times C \times 1.6485}{D \times 10^4} \quad (5)$$

where:
A = 0.0141 *N* $AgNO_3$ used for sample, mL,
B = 0.0141 *N* $AgNO_3$ used for blank, mL,
C = Cl/mL of titrant, µg,
D = weight of sample, g (see 38.1), and
1.6485 = conversion Cl (MW = 35.45) to NaCl (MW = 58.45); and 58.56/35.45 = 1.6485.

40. Report

40.1 Report the soluble chloride as NaCl to the nearest 0.01 %.

41. Precision and Bias

41.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 8):

41.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.00068% absolute with 32 df. The 95 % limit for the difference between two such determinations is 0.002 % absolute.

41.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.00035 % absolute with 16 df. The 95 % limit for the difference between two such averages is 0.001 % absolute.

41.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0012 % absolute with 7 df. The 95 % limit for the difference between two such averages is 0.004 % absolute.

41.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 8—These precision estimates are based on an interlaboratory study performed in 1993 on two samples of acid-grade fluorspar containing approximately 0.001 and 0.002 % sodium chloride. One analyst in each of eight laboratories performed duplicate determinations on each of two days for a total of 64 determinations.[5] Practice E 180 was used in developing the precision data.

42. Ion Chromatography Procedure, Scope

42.1 This test method covers the ion-chromatography determination of trace quantities of soluble chloride as µg/g (ppm) NaCl.

43. Summary of Test Methods

43.1 Soluble chloride is extracted from fluorspar with hot water, the extract made to volume, filtered, and then the chloride concentration is determined by ion chromatography.

44. Apparatus

44.1 *Balance*, capable of weighing to the nearest 0.1 g.

44.2 *Volumetric Flask*, 250-mL.

44.3 *Filter Medium*, chloride-free, 0.45-µm pore size, or less. (Gelman IC Acrodiscs fitted to a syringe work well.)

44.4 *Ion Chromatographic System*, able to produce baseline separation of fluoride, chloride, nitrate, phosphate, and sulfate.[7]

45. Reagents

45.1 *Chloride Standard*[8]—Dilute the standard with deionized water to a chloride concentration within the linear range of the detector and near the chloride level in the sample extract.

45.2 *Deionized Water*, chloride-free.

46. Hazards

46.1 See 1.3 and 1.4.

[7] A system known to produce adequate separation includes a DIONEX Model 20101 Ion Chromatograph equipped with a CDM-2 detector set at 10 µS; a DIONEX AS4A anion column, AG4A guard column and ASRS suppresser column; an eluant consisting of 1.7 mM $NaHCO_3$ in 1.8 mM Na_2CO_3; isocratic elution at 2.0 mL/min; a 50-µL sample injection.

[8] Use DIONEX Five Anion Standard Part No. 037157, or similar.

47. Procedure

47.1 Weigh 25 g of sample (previously dried to constant weight at 105 to 110°C) to the nearest 0.1 g into a 250-mL volumetric flask. Add 200 mL of hot (near boiling) deionized water to the flask. Using a magnetic stirrer, stir the sample for 1 h.

47.2 Cool the sample to room temperature under running water, make to volume with deionized water, then mix well.

47.3 Allow most of the fluorspar to settle (15 to 20 min), then filter a portion of the solution through a chloride-free, fine-porosity (0.45 µm, or less) filtered medium.

47.4 Chromatograph a portion of the filtrate, then compare the area of the resultant chloride peak to that of a chloride standard similarly chromatographed.

NOTE 9—If the chloride level of the filtrate is such that the resultant peak is outside the linear range of the detector, dilute the extract appropriately with deionized water and rechromatographed.

48. Calculation

48.1 Calculate the soluble chloride concentration as µg/g (ppm) NaCl as follow:

$$\text{Soluble chloride as NaCl, µg/g (ppm)} = \frac{A \times B \times 1.6485 \times 9.60 \times C}{D} \quad (6)$$

where:

A	=	area of sample peak,
B	=	µg/g chloride in the standard,
1.6485	=	conversion Cl (MW 35.45) to NaCl (MW 58.45) = 58.45/35.45 = 1.6485,
9.60	=	250/25 × 0.96,
250/25	=	dilution factor,
0.96	=	adjustment to dilution factor required since 25 g of sample displaces approximately 10 mL water,
C	=	any additional dilution factor needed to keep the Cl peak within the linear range of the detector, and
D	=	area of standard peak.

49. Report

49.1 Report soluble chloride as NaCl to the nearest 0.1 µg/g (ppm).

50. Precision and Bias

50.1 *Precision*—Use the following criteria for judging the acceptability of results (see Note 10):

50.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 1.26 µg/g with 18 df. The 95 % limit for the difference between two such determinations is 3.53 µg/g.

50.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 1.08 µg/g with 9 df. The 95 % limit for the difference between two such averages is 3.02 µg/g.

50.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 2.26 µg/g with 8 df. The 95 % limit for the difference between two such averages is 6.32 µg/g.

50.1.4 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 10—These precision estimates are based on an interlaboratory study performed in 1995 on one sample of acid-grade fluorspar containing approximately 15 µg/g of sodium chloride. One analyst in each of ten laboratories performed duplicate determinations on each of two days for a total of 40 determinations.[5] Practice E 180 was used in developing the precision data.

CALCIUM CARBONATE

51. Scope

51.1 This test method covers the determination of calcium carbonate in the range from 0 to 2 %.

52. Summary of Test Method

52.1 Calcium carbonate is extracted from fluorspar with dilute acetic acid; the extract is made alkaline with potassium hydroxide, and then calcium is titrated with disodium ethylenediaminetetraacetate (EDTA) solution using hydroxynaphthol blue as an indicator and calculated as calcium carbonate.

53. Apparatus

53.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

53.2 *Beakers*, 600, 400, 250, and 150-mL glass, unscratched, and watchglass covers.

53.3 *Graduated Cylinders*, 100, 25, and 10-mL.

53.4 *Stirring Rod*, borosilicate glass, unscratched.

53.5 *Steam Bath*.

53.6 *Glass Filter Funnel*.

53.7 *Mortar and Pestle*, 102-mm (4-in.) diameter, agate.

53.8 *Buret*, Class A, 50-mL, 0.1-mL division, polytetrafluoroethylene stopcock.

53.9 *Volumetric Flask*, 1-L.

53.10 *Hot Plate*, stirrer.

53.11 *Pipet*, 50-mL.

54. Reagents

54.1 *Acetic Acid Solution* (100 mL/L)—See 17.1.

54.2 *Ashless Cellulose Filter Aid*—Whatman accelerator powder,[6] or equivalent.

54.3 *Filter Paper*, 9-cm—See 17.4.

54.4 *Ethanol*—Pure or denatured.

54.5 *Filter Pulp Slurry* (40 g/L)—See 17.7.

54.6 *Litmus Paper*.

54.7 *Hydroxynaphthol Blue Indicator*—Fisher Scientific H346-100,[9] calcium indicator, or equivalent.

54.8 *Potassium Hydroxide* (30 % weight/volume)—Dissolve 300 g of potassium hydroxide (KOH) in water and dilute to 1 L; mix well. Store in a plastic bottle.

54.9 *Triethanolamine Solution* (1 + 1)—Mix 50 mL of triethanolamine ($NC_6H_{15}O_3$) with 50 mL of water; mix well.

[9] Correct American Chemical Society name is (ethylenedinitrilo) tetraacetic acid disodium salt dihydrate.

54.10 *Calcium Carbonate* ($CaCO_3$)—High purity, minimum 99.95 %.

54.11 *Hydrochloric Acid* (1 + 10)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 10 volumes of water.

54.12 *Disodium Ethylenediaminetetraacetate (EDTA) Standard Solution* (0.025 M)—Dissolve 9.3062 g of disodium ethylenediaminetetraacetate dihydrate ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$)[9] in water. Transfer the solution to a 1-L volumetric flask; dilute to volume with water; and mix well. Standardize as follows.

54.12.1 Dry 3 g of $CaCO_3$ in a 110°C oven for 1 h. Remove from oven and allow to cool in a desiccator. Weigh 2.4970 g of the dried $CaCO_3$ into a 600-mL beaker, cautiously add 75 mL of 1 + 10 HCl to the beaker, cover, and warm gently to dissolve the $CaCO_3$. Cool the solution and transfer into a 1-L volumetric flask, dilute to volume with water, and mix well (solution concentration: 1 mL = 1.0000 mg of Ca).

54.12.2 Pipet 50 mL of the solution prepared in 54.12.1 into a 400-mL beaker, add 5 mL of 1 + 1 triethanolamine to the beaker, and dilute to 200 mL with water. Dropwise, add 30 % KOH until the solution tests neutral with litmus paper. Add an additional 10 mL of 30 % KOH to the solution and mix well.

54.12.3 Add 0.5 g hydroxynaphthol blue indicator and titrate immediately with 0.025 *M* EDTA solution to a blue end point. Record *A*, the millilitres of EDTA required for the titration.

$$\text{calcium oxide equivalent of EDTA in g CaO/mL EDTA} = 50.0/A \times 1.3992 \times 0.001 = F \quad (7)$$

where:

50.0 = mL of $CaCO_3$ solution used in titration,
A = mL of EDTA solution used for titration,
1.3992 = conversion factor for calcium to calcium oxide, MW CaO = 56.08/MW Ca = 40.08, and
0.001 = conversion of mg to g.

54.12.4 Standardize the EDTA solution in triplicate using the steps described in 54.12.2 and 54.12.3, and average the three results to the nearest 0.000001 g/mL.

55. Hazards

55.1 See 1.3 and 1.4.

56. Procedure

56.1 Transfer 8 to 10 g of sample (previously dried to constant weight at 105 to 110°C) into a mortar. Grind with a pestle until the particle size is 100 to 500 mesh.

56.2 Weigh 1.0 g of the ground sample to the nearest 0.0001 g, and transfer it to a 150-mL beaker.

56.3 Wet the sample with 1 mL of ethanol, then add 15 mL of acetic acid (100 mL/L) to the beaker.

56.4 Add a glass stirring rod to the beaker, cover with a watchglass, and place on a steam bath.

56.5 Heat for 30 ± 1 min, stirring every 5 min.

56.6 Remove from the steam bath, add 5 mL of filter pulp slurry to the beaker, cover, and allow to sit for approximately 12 h.

56.7 Gravity-filter the solution through medium porosity filter paper.

56.8 Rinse the beaker several times with minimal portions of hot water (total wash water approximately 35 mL), filtering each wash through the same filter paper.

56.9 Add 5 mL of triethanolamine solution to the filtrate in a 250-mL beaker.

56.10 Dropwise, add 30 % KOH to the solution until it tests neutral with litmus paper.

56.11 Add 10 mL additional 30 % KOH; mix well.

56.12 Add 0.5 g of hydroxynaphthol blue indicator to the solution; mix well.

56.13 Titrate the solution with standardized 0.025 *M* EDTA solution to a blue end point. Record *C*, the millilitres of EDTA required for the titration.

57. Calculation

$$\%\ CaCO_3 = \frac{[(C \times F) - 0.0010] \times 1.7848 \times 100}{B} \quad (8)$$

where:

C = mL of 0.025 *M* EDTA solution used in titration (56.13),
B = sample weight (56.2),
F = factor representing g CaO/mL EDTA (54.12.4),
0.0010 = correction for calcium fluoride dissolved in the acetic acid treatment, estimated to be 0.0010 g/g of sample, and
1.7848 = conversion factor for CaO (MW = 56.08) to $CaCO_3$(MW = 100.09) (that is, 100.09/56.08 = 1.7848).

58. Report

58.1 Report the percent calcium carbonate to the nearest 0.01 %.

59. Precision and Bias

59.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 11):

59.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0148 % absolute at 38 df. The 95 % limit for the difference between two such determinations is 0.04 % absolute.

59.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0156 % absolute at 19 df. The 95 % limit for the difference between two such averages is 0.04 % absolute.

59.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0910 % absolute at 8 df. The 95 % limit for the difference between two such averages is 0.25 % absolute.

59.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 11—These precision estimates are based on an interlaboratory study performed in 1994 on two samples of acid-grade fluorspar containing approximately 0.55 and 0.79 % calcium carbonate. One analyst in each of ten laboratories performed duplicate determinations on each of two days for a total of 80 determinations.[5] Practice E 180 was used in

developing the precision data.

PHOSPHORUS

60. Scope

60.1 This test method covers the determination of total phosphorus.

61. Summary of Test Method

61.1 The sample is dissolved in nitric acid, fumed with perchloric acid, then reacted with ammonium molybdate to form heteropoly phosphomolybdate. The phosphomolybdate is reduced with hydrazine sulfate to form the molybdenum blue complex, which is measured at 650 nm or 825 nm, depending on the concentration of analyte. Hydrobromic acid is added to eliminate interference by arsenic.

62. Apparatus

62.1 *Spectrometer*, capable of measurements at 650 nm and 825 nm.

62.2 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

62.3 *Beakers*, 400-mL.

62.4 *Graduated cylinders*, 10-mL, 25-mL, 50-mL, 100-mL.

62.5 *Bunsen burner*, hot plate, hot water bath.

62.6 *Funnel*, No. 40 Whatman filter paper, 11-cm.

62.7 *Volumetric flasks*, 100-mL, 500-mL, 1000-mL, borosilicate glass, volumetric.

62.8 *Pipets*, 1-mL, 10-mL, 20-mL, 50-mL.

62.9 *Erlenmeyer flask*, 250-mL.

63. Reagents

63.1 *Ammonium Molybdate Solution (20 g/L)*—Add 300 mL of H_2SO_4 to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{27}\cdot 4H_2O$), dilute to 1 L, and mix.

63.2 *Hydrazine Sulfate Solution (1.5 g/L)*—Prepare fresh daily. Dissolve 1.5 g of hydrazine sulfate ($(NH_2)_2\cdot H_2SO_4$) in water, dilute to 1 L, and mix.

63.3 *Ammonium Molybdate—Hydrazine Sulfate Solution*—Dilute 250 mL of Ammonium Molybdate Solution (20 g/L) to 600 mL, add 100 mL of Hydrazine Sulfate Solution (1.5 g/L), dilute to 1 L and mix well.

63.4 *Phosphorus Stock Solution (1 mL = 1.0 mg P)*—Transfer 2.292 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4), previously dried to a constant weight at 105°C, to a 500-mL volumetric flask; dissolve in about 100 mL of water, dilute to volume, and mix.

63.5 *Phosphorus Standard A (1 mL = 0.1 mg P)*—Pipet 50 mL of Phosphorus Stock Solution into a 500-mL volumetric flask, add 50 mL of $HClO_4$(1 + 5), dilute to volume, and mix.

63.6 *Phosphorus Standard B (1 mL = 0.01 mg P)*—Pipet 10 mL of Phosphorus Stock Solution into a 1-L volumetric flask, add 100 mL of $HClO_4$(1 + 5), dilute to volume, and mix.

63.7 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

63.8 *Hydrochloric Acid (1 + 1)*—Add 100 mL of concentrated HCl to 200 mL of water and mix well.

63.9 *Hydrochloric Acid (1 + 100)*—Add 1 mL of concentrated HCl to 100 mL of water and mix well.

63.10 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

63.11 *Perchloric Acid (sp gr 1.54)*—Concentrated perchloric acid ($HClO_4$).

63.12 *Perchloric Acid (1 + 5)*—Add 100 mL of concentrated perchloric acid to 500 mL of water and mix well.

63.13 *Ferric Chloride Solution (20 g/L)*—Add 20 g of ferric chloride to a 1-L volumetric flask, add 10 mL of concentrated HCl, dilute to mark with water, and mix well.

63.14 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

63.15 *Ammonium Chloride Solution (20 g/L)*—Add 20 g of ammonium chloride to a 1-L volumetric flask, add water, dilute to mark, and mix well.

63.16 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

63.17 *Sulfuric Acid (3 + 37)*—Add 30 mL of concentrated sulfuric acid to 370 mL of water and mix well.

63.18 *Sodium Sulfite*.

63.19 *Sodium Sulfite Solution (100 g/L)*—Dissolve 100 g of sodium sulfite in water, dilute to 1 L and mix.

63.20 *Hydrobromic Acid (sp gr 1.490)*—Concentrated hydrobromic acid (HBr).

63.21 *Hydrobromic Acid (1 + 4)*—Add 100 mL of concentrated HBr to 400 mL of water and mix well.

64. Hazards

64.1 See 1.3 and 1.4.

65. Preparation of Calibration Curve

65.1 *0.05–0.30 mg P/100 mL Calibration Range:*

65.1.1 Pipet 5-, 10-, 15-, 20-, 25-, and 30-mL portions of Phosphorus Standard A (1 mL = 0.1 mg *P*) into separate 100-mL volumetric flasks.

65.1.2 Add 20 mL of concentrated perchloric acid to each flask, dilute to volume, and mix well.

65.1.3 Pipet 10 mL of each solution into separate 100-mL volumetric flasks.

65.1.4 Add 15 mL of sodium sulfite (100 g/L) to each flask, swirl and gently boil the solutions for approximately 30 seconds on a hot plate in a hood.

65.1.5 Add 50 mL of ammonium molybdate-hydrazine sulfate solution to each flask and heat the flasks in a boiling-water bath for approximately 20 minutes.

65.1.6 Quickly cool the solutions in an ice bath, dilute each to 100 mL with water, and mix well.

65.1.7 Prepare a reagent blank as follows: Transfer 12 mL of $HClO_4$(1 + 5) to a 100-mL flask, then continue from 65.1.4.

65.1.8 Using water as a reference, record the absorbance of each standard solution and the reagent blank at 650 nm.

65.1.9 Prepare a calibration curve by plotting the absorbances of the standards (corrected for reagent blank) versus mg of P/100 mL of solutions.

65.2 *0.005–0.03 mg P/100 mL Calibration Range*:

65.2.1 Pipet 5-, 10-, 15-, 20-, 25-, and 30-mL portions of Phosphorus Standard B (1 mL = 0.01 mg *P*) into separate 100-mL volumetric flasks.

65.2.2 Develop the color of these standards following 65.1.2-65.1.6.

65.2.3 Prepare a reagent blank as follows: Transfer 12 mL of $HClO_4$(1 + 5) to a 100-mL flask, then continue from 65.1.4.

65.2.4 Using water as a reference, record the absorbance of each standard solution and the reagent blank at 825 nm.

65.2.5 Prepare a calibration curve by plotting the absorbances of the standards (corrected for reagent blank) versus mg of P/100 mL of solution.

66. Procedure

66.1 Weigh 1.0000 g of dried fluorspar to 0.0001 g and transfer to a 400-mL beaker. Weight = *W*.

66.2 Add 10 mL of HNO_3, 10 mL of $HClO_4$, cover the beaker with a watch glass, and heat the mixture on a hot plate. When the sample is nearly totally dissolved, remove from the hot plate, cool, then carefully wash down the watch glass and the sides of the beaker with water. Carefully evaporate the sample to near dryness on a hot plate.

66.3 Remove from heat, cool, add 10 mL of concentrated HNO_3 and 100 mL of water and heat the solution on a hot plate to dissolve the salts.

66.4 Remove the beaker from the hot plate and cool. Add 5 mL of ferric chloride solution to the beaker, then add ammonium hydroxide until iron precipitates.

66.5 Boil the solution for 3 minutes on a hot plate then gravity filter through No. 40 Whatman filter paper. Discard the filtrate.

66.6 Add 20 mL of HCl (1 + 1) to dissolve residual matter then transfer the residue to the filter, collecting the filtrate in a 250-mL Erlenmeyer flask.

66.7 Wash the beaker with 20-mL portions of hot water, transferring each wash to the filter cake. Continue the washings until there is no yellow color left on the filter paper (3–5 washings); collect all washings in the Erlenmeyer flask.

66.8 Add 10 mL of $HClO_4$ to the flask, heat on a hot plate until fumes appear, then heat one minute more.

66.9 Cool the flask, then add 20 mL of HBr (1 + 4). Heat on a hot plate until strong white fumes appear, then for one minute more.

66.10 Cool the flask, wash the contents into a 100-mL volumetric flask with water, make to volume and mix well. Pipet 20 mL of this solution into a second 100-mL volumetric flask.

66.11 Add 15 mL of sodium sulfite solution and gently boil the solution for approximately 30 seconds on a hot plate in a hood.

66.12 Add 50 mL of ammonium molybdate-hydrazine sulfate solution and heat the flask in a boiling water bath for approximately 20 minutes.

66.13 Cool the solution, dilute to 100 mL with water, and mix well.

66.14 Read the absorbance of the solution at 650 nm or 825 nm as appropriate; Absorbance = *A*.

66.15 Similarly determine the absorbance of a blank solution containing all reagents, but no sample; Absorbance = *B*.

67. Calculation

67.1 Using the calibration curves or a straight-line formula, determine the concentration of *P* in mg/100 mL equivalent to the blank-corrected absorbance (*A* − *B*); concentration = *C*.

$$P\ (\%) = \frac{C \times 100 \times 100 \times 5}{W \times 1000} = \frac{50 \times C}{W} \quad (9)$$

where:

C	=	mg P/100 mL, equivalent to the blank-corrected sample absorbance,
W	=	sample weight in g,
100	=	original sample volume in mL,
100	=	conversion factor to percent,
5	=	dilution factor (100 mL/20 mL), and
1000	=	conversion factor, milligrams to g.

68. Report

68.1 Report results to the nearest 0.001 %.

68.2 Minimum reportable quantity is 0.001 %.

69. Precision and Bias

69.1 Studies are planned to determine the precision of this test method.

69.2 The bias of this test method cannot be determined unless a suitable reference material becomes available.

ARSENIC

70. Scope

70.1 This test method covers the determination of total arsenic.

71. Summary of Test Method

71.1 The sample is oxidized with bromine and nitric acid then arsenic is determined using Graphite-Furnace Atomic Absorption Spectroscopy.

72. Apparatus

72.1 *Atomic Absorption Spectrometer*, equipped with a graphite furnace, Zeeman background correction, and an arsenic electrodeless discharge lamp.[10]

72.2 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

72.3 *Volumetric flasks*, 100-mL, 500-mL, borosilicate glass, volumetric.

72.4 *Pipets*, 1-mL, 2-mL, 10-mL.

72.5 *Phillips beaker*, 250-mL with watch glass cover.

73. Reagents

73.1 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

73.2 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

73.3 *Palladium Sponge*.

73.4 *Palladium Solution (5 g/100 mL)*—Weigh 5.0 g of Pd metal into a 250-mL beaker. Add 25 mL concentrated HCl and 25 mL concentrated HNO_3. Heat until completely dissolved. Cool, then dilute to 100 mL with water. Mix well.

73.5 *Magnesium Nitrate*—Alfa Puratronic or equivalent.

73.6 *Magnesium Nitrate Solution (1 g/100 mL)*—Dissolve 1.0 g of $Mg(NO_3)_2$ in water, then make to 100 mL. Mix well.

[10] A system known to produce adequate results includes: a Perkin-Elmer Model PE 5000 Spectrometer and a Perkin-Elmer Model 6100 HGA Graphite Furance.

73.7 *Bromine/Carbon Tetrachloride (2 + 3)*—Mix 500 mL of Br_2 and 750 mL of CCl_4.

73.8 *Palladium/Magnesium Nitrate Matrix Modifier*—Dilute 6.0 mL of 5 g/100 mL Pd Solution and 10.0 mL of 1 g/100 mL $Mg(NO_3)_2$ solution to 100 mL with water and mix well.

73.9 *Arsenic Stock Solution (1000 mg/L)*—Fisher Cat. No. SA449, or equivalent.

73.10 *Arsenic Stock Solution (100 mg/L)*—Pipet 10.0 mL of 1000 mg/L Stock Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and 10 mL of concentrated HCl and dilute to volume with water. Mix well.

73.11 *Arsenic Stock Solution (10 mg/L)*—Pipet 10.0 mL of 100 mg/L Stock Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

73.12 *Arsenic Standard Solution (1.0 mg/L)*—Pipet 10.0 mL of 10 mg/L Stock Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

73.13 *Arsenic Standard Solution (0.10 mg/L)*—Pipet 10.0 mL of 1 mg/L Standard Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

73.14 *Arsenic Standard Solution (0.01 mg/L)*—Pipet 10.0 mL of 0.10 mg/L Standard Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

74. Hazards

74.1 See 1.3 and 1.4.

75. Procedure

75.1 Weigh 0.100 g of dried fluorspar to 0.0001 g and transfer to a 250-mL Phillips beaker.

75.2 Add 10 mL of Br_2/CCl_4(2 + 3), swirl to mix, cover the beaker with a watch glass, and allow to sit in a fume hood for 15 min.

75.3 Add 10 mL of HNO_3 to the sample, swirl to mix, cover, and allow the sample to sit in a fume hood for 15 min.

75.4 Heat on a hot plate at low-medium heat until brown bromine fumes are no longer visible, then continue digestion until the sample volume is approximately 5–8 mL.

75.5 Rinse down the sides of the beaker and the watch glass with approximately 50 mL of water.

75.6 Cover the sample and heat to just boiling on a hot plate. Cool.

75.7 Using water, quantitatively transfer the sample to a 100-mL volumetric flask, make to volume, and mix well.

75.8 Determine the sample's absorbance using Graphite-Furnace Atomic Absorption Spectroscopy using the following conditions:

NOTE 12—The following conditions are specific for the Perkin-Elmer equipment described in 72.1. If other equipment is used for the analysis, conditions will have to be changed appropriately.

Wavelength: 193.7 nm
Slit width: 0.7 nm
Integration time: 5 s
Lamp: Electrodeless discharge, set at 330 ma
Measurement mode: Absorbance of peak area
Gas: Argon
Zeeman background correction: On
Furnace settings:

Step	Temperature,° C	Ramp	Hold Time, s	Read
1	150	1	60	
2	400	10	30	
3	2400	0	5	X
4	2600	...	5	

75.9 Similarly determine the absorbances of a reagent blank and appropriate standards.

76. Calculation

$$\mu g/g\ (\text{ppm wt/wt})\ \text{As} = \frac{A_1 \times C \times 100}{A_2 \times 0.1} = \frac{A_1 \times C \times 1000}{A_2} \quad (10)$$

where:
A_1 = blank-corrected sample absorbance,
C = concentration of standard in µg/g,
100 = sample volume in mL, and
0.1 = sample weight in g.

77. Report

77.1 Report results to the nearest 1 µg/g (ppm).

77.2 Minimum reportable quantity is 1 µg/g (ppm).

78. Precision and Bias

78.1 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results, each the average of duplicates, obtained by the same analyst on different days, has been estimated to be 2 µg/g with 41 df. The 95 % limit for the difference between two such averages is 6 µg/g.

NOTE 13—This precision estimate is based on the analysis of a single sample in one laboratory over the period from May 1995 to October 1996.

78.2 The bias of this test method cannot be determined unless a suitable reference material becomes available.

MIXED OXIDES (R_2O_3)

79. Scope

79.1 This test method covers the determination of percent mixed oxides (R_2O_3).

80. Summary of Test Method

80.1 The acetic acid extract from the determination of percent silica (see 19.8) is oxidized with hydrochloric and nitric acids, then treated with ammonium hydroxide to precipitate metal hydroxides. This precipitate is combined with the ammonium hydroxide precipitate from the determination of percent calcium fluoride (see 29.17), the combined precipitates are calcined at 800°C, then the residue is weighed and calculated as percent mixed oxides (R_2O_3).

81. Apparatus

81.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

81.2 *Desiccator* desiccant (silica gel is suitable).

81.3 *Muffle furnace*, capable of maintaining a temperature of at least 800°C.

81.4 *Platinum crucible*, 30-mL.
81.5 *Graduated cylinders*, 10-mL, 50-mL.

82. Reagents

82.1 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).
82.2 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).
82.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).
82.4 *Filter Paper*, 9-cm, low ash, acid-washed, medium-porosity, able to retain 8-µm particles.

83. Hazards

83.1 See 1.3 and 1.4.

84. Procedure

84.1 Transfer the filtrate from the determination of percent silica (see 19.8) to a 250-mL beaker, and add 5 mL of HCl and 1 mL of HNO_3 to the beaker.
84.2 Boil the solution for 2–3 min, remove the beaker from the heat, and allow to cool.
84.3 Add 3–5 drops of 0.5 % phenolphthalein indicator solution to the sample. While stirring, add ammonium hydroxide to the solution until it turns pink, then boil the solution for one minute more.
84.4 Allow the solution to cool, then gravity filter it through medium-porosity filter paper.
84.5 Wash the filter cake with about 50 mL of hot water.
84.6 Heat a 30-mL platinum crucible at 800°C for 20 min. Cool to room temperature in a desiccator, then weigh to the nearest 0.0001 g; weight = *C*.
84.7 Combine the above filter paper and filter cake with the filter paper and filter cake from the ammonium hydroxide precipitate from the determination of percent calcium fluoride (see 29.17) in the crucible, then place the crucible in a muffle furnace and carefully ignite at 800°C.
84.8 After all the paper has burned off, heat the crucible for 5 min more.
84.9 Place the crucible in a desiccator to cool, then weigh to 0.0001 g; weight = *B*.

85. Calculation

$$\% \text{ mixed oxides } (R_2O_3) = \frac{(B - C)}{A} \times 100 \qquad (11)$$

where:
B = weight of crucible plus ash, see 84.8,
C = weight of crucible, see 84.6,
A = weight of sample, see 18.2, and
100 = conversion to percent.

86. Report

86.1 Report results to the nearest 0.01 %.
86.2 Minimum reportable quantity is 0.01 %.

87. Precision and Bias

87.1 Studies are planned to determine the precision of this test method.
87.2 The bias of this test method cannot be determined unless a suitable reference material becomes available.

SULFIDE SULFUR

88. Scope

88.1 This test method covers the determination of sulfide sulfur in the range from 0.001 to 0.2 %.

89. Summary of Test Method

89.1 Fluorspar is mixed with HCl, boric acid, and amalgamated zinc. Hydrogen sulfide is then distilled from the mixture. The evolved hydrogen sulfide is carried off by a stream of oxygen-free nitrogen or argon, and collected in zinc acetate solution. Hydrochloric acid and iodine are added to the zinc acetate solution, and the excess iodine is back titrated with sodium thiosulfate.

90. Apparatus

90.1 *Analytical Balance*, capable of weighing to the nearest 1 mg.
90.2 *Sulfide Evolution Apparatus*, consisting of a nitrogen or argon gas cylinder with appropriate regulator, flow meter, gas washing bottles (250 mL), one with alkaline pyrogallol and one with zinc acetate solution (30 g/L), separatory funnel, 500-mL three-neck flask, condenser, gas washing bottle (125 mL), and connecting glass tubing (see Fig. 1).

NOTE 14—Hydrofluoric acid produced by the reaction between fluorspar and hydrochloric acid gradually corrodes the 500-mL flask. After each run, tap the bottom of the flask gently on the table top to make certain that it is still safe to use. Also, rinse down the inside of the condenser after each run to remove any globules of mercury that may be deposited there.

90.3 *Graduated Cylinder*, 100-mL, glass.
90.4 *Pipet*, 10-mL.
90.5 *Heating Mantel*, for 500-mL round-bottom flask.
90.6 *Micro-Burette*, readable to 0.01 mL.

91. Reagents

91.1 *Zinc, 20 Mesh*—Clean by treating for a few minutes with 1:19 HCl; decant off the HCl just prior to amalgamation.
91.2 *Amalgamated Zinc*—Dissolve 2 g of mercuric chloride in 50 mL of water, and add a few drops of HCl to acidify the solution. Heat to 50–60°C to dissolve any salt. Add 50 g of clean zinc to the heated solution. Allow the mixture to stand for 3 to 5 min, stirring occasionally. Pour off the supernatant liquid, and wash the zinc at least 5 times by decantation to remove excess mercuric chloride. Do Not allow the amalgamated zinc to dry. Store under water, and weigh wet.
91.3 *Hydrochloric Acid (1 + 2)*—Dilute 1 vol of concentrated HCl with 2 vol of water.
91.4 *Hydrochloric Acid (1 + 19)*—Dilute 10 vol of concentrated HCl with 190 vol of water.
91.5 *Digestion Acid*—Mix 400 mL of concentrated HCl with 1000 mL of water. Add 1 g of chromic chloride or 0.33 g of chrome metal to the solution, and mix well until the chrome dissolves.
91.6 *Boric Acid*.
91.7 *Starch Solution*, 1 %.
91.8 *Nitrogen or Argon*, oxygen-free.

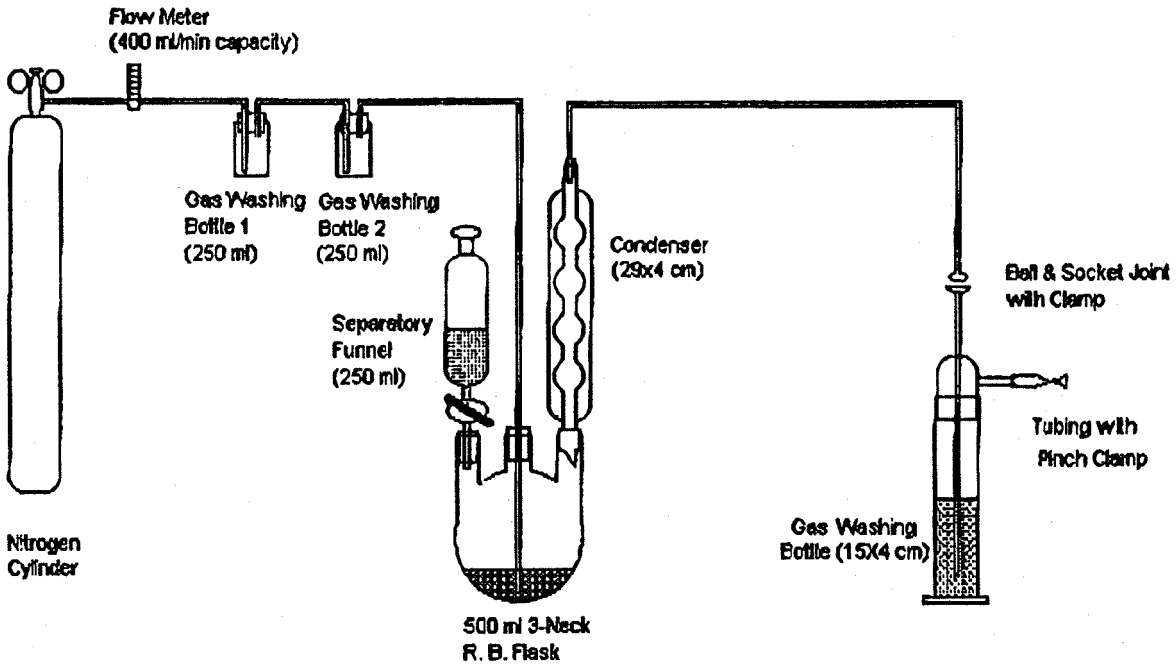

FIG. 1 Sulfide Distillation Apparatus

91.9 *Iodine, 0.005 N*—Prepare fresh. Pipet 10 mL of standard 0.1 N iodine to 200 mL with water, and mix well.

91.10 *Zinc Acetate Solution (30 g/L)*—Dissolve 30 g of zinc acetate and 6 mL of glacial acetic acid in water and dilute to 1000 mL.

91.11 *Sodium Thiosulfate, Standard Solution (0.01 N)*—Prepare fresh. Pipet 20 mL of standard 0.1 N sodium thiosulfate solution into a 200-mL volumetric flask, dilute to the mark with water, and mix well.

91.12 *Alkaline Pyrogallol*—Add 50 mL of 10 % aqueous Pyrogallol to 200 mL of 50 % weight/vol aqueous KOH. Mix well. Store in a tightly-capped container until used.

92. Hazards

92.1 See 1.3 and 1.4.

93. Procedure

93.1 Assemble the apparatus shown in Fig. 1, making certain that all Teflon® stoppers and connections are tight.

NOTE 15—The apparatus operates under a slight positive pressure, and therefore, all connections must be tight. Even a small leak may result in a serious loss of hydrogen sulfide.

93.2 Place 50 mL of zinc acetate solution into the gas washing bottle.

93.3 Weigh 3 g of dried sample to the nearest 0.001 g, and transfer it to the 500-mL three-neck flask; record the sample weight as *A*.

93.4 Add 2.5 g of amalgamated zinc and 2 g of boric acid to the flask.

93.5 Connect the flask to the gas train, and with the pinch clamp open, adjust the nitrogen flow to about 100 mL/min, and purge the apparatus for 10 min.

93.6 Add 85 mL of digestion acid to the separatory funnel.

93.7 Open the separatory funnel stop cock. Using a pipet bulb, force about 80 mL of the acid into the 500-mL flask, making certain that no air enters the flask. Close the stop cock.

93.8 Boil the contents of the flask for 30 min, adjusting the temperature so that froth about half-fills the flask, but does not rise high enough to enter the neck of the flask.

93.9 Carefully disconnect the delivery tube from the condenser, at the ball and socket joint, and seal the outlet tube on the gas washing bottle with tubing and a clamp.

93.10 Remove cap from gas washing bottle. Quickly add 10.0 mL of 0.005 N iodine solution and 10 mL of HCl (1+2) solution to the zinc acetate collection solution in the gas washing bottle. Replace cap. Keeping the outlet tube sealed, allow the mixture to stand for about 15 min.

93.11 Remove cap, open pinch clamp, and rinse the gas inlet tube carefully, collecting the washings in the bottle. Take care that all the zinc sulfide adhering to the inlet tube has been dissolved completely.

93.12 Using 0.005 N sodium thiosulfate, back-titrate the excess iodine, adding 1 mL of starch solution just before the end-point is reached. Continue titrating to the clear end-point. Record *B*, the millilitres of 0.005 N sodium thiosulfate needed for the titration.

93.13 Similarly, determine a blank, using all of the same reagents, but no sample. Record *C*, the millilitres of 0.005 N sodium thiosulfate needed for the blank.

94. Calculation

94.1 Calculate:

$$\% \text{ sulfide sulfur} = \frac{(C - B) \times N \times 0.016 \times 100}{A} \quad (12)$$

where:

B = sodium thiosulfate used for the sample, mL,
C = sodium thiosulfate used for the blank, mL,
A = sample weight, g,
0.016 = milliequivalent weight of sulfur, and

N = normality of sodium thiosulfate.

95. Report

95.1 Report the concentration of sulfide sulfur to the nearest 0.0001 %.

95.2 Minimum reportable quantity is 0.0001 %.

96. Precision and Bias

96.1 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results, each the average of duplicates, obtained by the same analyst on different days, has been estimated to be 0.0003 % with 17 df. The 95 % limit for the difference between two such averages is 0.0008 %.

NOTE 16—This precision estimate is based on the analysis of a single sample in one laboratory over the period from April to October 1996.

96.2 *Bias*—The bias of this test method cannot be determined unless a suitable reference material becomes available.

97. Keywords

97.1 arsenic; calcium carbonate; calcium fluoride; fluorspar; mixed oxides (R_2O_3); moisture; phosphorus; silica; soluble chloride; sulfide sulfur; volatiles