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Standard Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures)[1,2]

This standard is issued under the fixed designation D 3269; 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.

This standard has been approved for use by agencies of the Department of Defense.

ε[1] NOTE—Footnotes were deleted editorially throughout in March 2001.

1. Scope

1.1 These test methods describe manual procedures for the determination of fluoride in various types of samples. The procedures outlined, consequently, are appropriate to the analysis of ambient air samples taken by diverse sampling techniques when properly applied.

1.2 The values stated in SI units are to be regarded as the standard.

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 10.7.1.3 and Ref **(9)**.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[3]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[4]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[4]

D 3267 Test Method for Separation and Collection of Particulate and Water-Soluble Fluorides in the Atmosphere (Filter and Impinger Method)[4]

D 3268 Test Method for Separation and Collection of Particulate and Gaseous Fluorides in the Atmosphere (Sodium Bicarbonate-Coated Glass Tube and Particulate Filter Method)[4]

D 3270 Test Methods of Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)[4]

E 1 Specification for ASTM Thermometers[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Terminology D 1356.

4. Summary of Test Methods

4.1 Fundamentally, isolation of the fluoride followed by analytis constitutes each of the methods. Because of the wide range of types of samples and the care required in the analysis to provide a representative sample, reliable isolation of the fluoride, and accurate measurement, the methods are prefaced by discussion of general precautions and sample preparation as applied to specific cases.

5. Significance and Use

5.1 These test methods may be used for the determination of the fluoride content of particulate matter and gases collected in the atmosphere by passive and active monitors, including plant material. The user is warned that the fluoride content of passive collectors (including plant materials) gives a qualitative or semiquantitative measure of atmospheric concentrations or deposition rates of fluorides.

6. Apparatus

6.1 *Crucible, nickel, inconel, or platinum.*

6.2 *Beakers, nickel or platinum.*

6.3 *Muffle Furnace.*

6.4 *Wiley Cutting Mill.*

[1] These test methods are under the jurisdiction of ASTM Committee D22 on Sampling and Anlysis of Atmospheres and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] These test methods were originally written by the Intersociety Committee on Methods for Ambient Air Sampling and Analysis and published as "Tentative Methods of Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Methods)" 12204-01-68T pp. 246–265, *Methods of Air Sampling and Analysis*, 1972, Parts A–F and 12202-01-72T, pp. 304–307, *Health Laboratory Science*, Vol 9, No. 4, October 1972. This revision has been adapted from "Methods of Air Sampling and Analysis," Intersociety Committee, edited by James P. Lodge, Jr., 3rd Edition, Lewis Publishers, Inc., 1989, pp. 344–346 and 352–356. The methods are presented here essentially as published. The individuals participating in the Intersociety Committee work and the sources of the methods are referenced in the publications cites.

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

[4] *Annual Book of ASTM Standards*, Vol 11.03.

[5] *Annual Book of ASTM Standards*, Vol 14.03.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6]

7.2 *Purity of Water*—Water shall be Type II reagent water conforming to Specification D 1193. Additionally, the water used in the sampling and analytical procedure shall be demonstrated by testing with a specific ion electrode or by concentration and photometric analysis to contain less than 0.005 µg/mL of F.

7.3 *Calcium Oxide*, (CaO), with known low fluoride concentration.

7.4 *Hydrochloric Acid*, (2 %)—Dilute 5 mL of hydrochloric acid (HCl, sp gr 1.19) to 100 mL with water.

7.4.1 *Hydrochloric Acid*, (4 %)—Dilute 10 mL of hydrochloric acid (HCl, sp gr 1.19) to 100 mL with water.

7.5 *Hydrogen Peroxide Solution*, (30 %), (H_2O_2).

7.6 *Nitric Acid*, (5 %)—Dilute 5 mL of nitric acid (HNO_3, sp gr 1.42) to 100 mL with water.

7.7 *Phenolphthalein Indicator Solution* (0.05 g/L)—Dissolve 0.5 g of phenolphthalein in 60 mL of ethyl alcohol and dilute to 1 L with water.

7.8 *Sodium Hydroxide* (10 %)—Dissolve 10.0 g of sodium hydroxide (NaOH) in water and dilute to 100 mL with water.

7.8.1 *Sodium Hydroxide* (20 %)—Dissolve 20.0 g of sodium hydroxide (NaOH) in water and dilute to 100 mL with water.

7.9 *Sodium Hydroxide Alcoholic Solution*, (1 *N*)—Dissolve 4 g of NaOH in 5 mL of water and dilute to 100 mL with ethyl, methyl, or Formula 30 denatured alcohol.

8. Sampling

8.1 See Practice D 1357 for general sampling procedures, and Test Methods D 3267 and D 3268 for procedures and guidelines applicable to sampling atmospheric fluorides.

9. General Precautions and Sample Preparation

9.1 *General Precautions*:

9.1.1 Fluorine is one of the more common elements and occurs in at least trace amounts in virtually all natural and manufactured materials. Contamination by extraneous fluoride may, therefore, come from such sources as sampling and laboratory apparatus, reagents, and from exposure to laboratory dust and fumes. Care must be exercised in the selection, purification, and testing of reagents and apparatus, and only minimal exposures of samples should be permitted.

9.1.2 Vessels used for evaporation, ashing, or caustic fusion of samples are first rinsed with warm, dilute HCl or HNO_3 (see 7.4 or 7.6) solution, then with water and air dried under clean toweling. Inconel crucibles used for fusion of ash may require additional cleaning by boiling in 10 % NaOH (see 7.8) solution for 1 h. Glassware is washed with hot detergent solution followed by a rinse in warm, dilute HCl or HNO_3 (see 7.4 or 7.6); it is finally rinsed with water and dried (see **Warning**). All sampling devices, containers, volumetric glassware, reagent solutions, and so forth, are stored under suitable conditions of protection from airborne dusts and fumes and are reserved for exclusive use in low-fluoride analysis. (**Warning—**The distilling flasks should be cleaned using only a brush and water. Repeated use of alkaline cleaning solution produces an etched surface that is difficult to clean and that tends to retain fluoride.)

9.1.3 Before proceeding with analysis of samples, blank determinations are repeated until satisfactorily low values (5 µg, or less, total fluoride per determination) are consistently obtained. Calibration standards are analyzed whenever new batches of reagent solutions are prepared. In addition, one blank and one standard determination are carried through the entire analytic procedure with each set of ten or fewer samples. If samples are handled in larger sets, the ratio of one blank and one standard per ten samples should be maintained.

9.2 *Sample Preparation*:

9.2.1 The techniques of sample recovery and preparation will vary, as described below, with the sampling method and equipment, and will also depend upon the procedures selected for isolation and measurement of fluoride. Until proof to the contrary is established, samples are assumed to contain fluoride in refractory forms in addition to the commonly encountered interfering materials. Many details involved in the determination of gaseous and particulate fluorides in the atmosphere and in vegetation are discussed by Pack, et al, **(1)**[7] and automatic apparatus for the determination of ambient atmospheric HF concentrations down to 0.1 ppb (v) has also been described **(2)**.

9.2.2 *Particulate Fluorides*:

9.2.2.1 Particulate matter collected in air sampling generally requires fusion with NaOH for conversion into soluble form before separation of fluoride by Willard-Winter distillation **(3)**. This treatment is also necessary for materials containing fluoride associated with aluminum, for materials high in silica, and for many minerals.

9.2.2.2 Transfer the sample-bearing paper filter to a resistant crucible (see 6.1), for example, nickel, platinum, or Inconel, moisten with water, and make alkaline to phenolphthalein (see 7.7) using CaO (see 7.3). After evaporation to dryness, ignite the paper in a muffle furnace at a temperature of 550 to 600°C until all carbonaceous material has been oxidized. Control combustion of filters of the membrane (cellulose ester) type by drenching with alcoholic NaOH (see 7.9) solution and igniting with a small gas flame.

9.2.2.3 Remove particulate matter, collected by electrostatic precipitation, from the surfaces of both electrodes with the aid of a rubber policeman and water. Make the resulting suspension alkaline to phenophthalein (see 7.7) with NaOH (see 7.9) solution and evaporate to dryness.

9.2.2.4 Integrated samples, that is, those containing both gaseous and particulate fluorides, that have been collected on

[6] *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.

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

glass fiber filters, are not amenable to fusion; filters are transferred directly to the distillation flask. Integrated samples collected in impingers are transferred to beakers made of nickel or other resistant materials, evaporated to dryness in the alkaline condition, and the residue ashed if organic matter is present.

9.2.2.5 Fuse the impinger sample, residue from ashing of a filter, or electrostatic precipitator catch, with 2 g of NaOH. Dissolve the cold melt in a few millilitres (mL) of water, add four or five drops of 30 % H_2O_2 (see 7.5) to oxidize sulfites to sulfates, and boil the solution to destroy excess peroxide. The sample solution is then ready for isolation of fluoride.

9.2.3 *Ambient Gaseous Fluorides, Dry Collectors*:

9.2.3.1 Treat filter papers impregnated with calcium-based fixative agents as described above for particulate fluorides, except that caustic fusion of the ashed residue is not required.

9.2.3.2 Filters impregnated with soluble alkalies are leached with water, as are fixative-coated beads or tubes. Evaporate the washings in a suitable vessel and maintain in an alkaline condition during reduction to a volume convenient for the subsequent fluoride separation procedure. Add four or five drops of 30 % H_2O_2 (see 7.5) and boil the solution to destroy excess peroxide.

9.2.3.3 Gaseous fluorides collected on glass fiber filters cannot be quantitatively removed by leaching with water. Transfer such filters directly to the flasks in which Willard-Winter distillations are to be conducted.

9.2.4 *Ambient Gaseous Fluorides, Wet Collectors*:

9.2.4.1 Transfer a sample collected in water or alkaline solution to a suitably sized vessel, make alkaline to phenolphthalein (see 7.7) with NaOH (see 7.9), and evaporate to the desired volume. Treat the solution with 30 % H_2O_2 (see 7.5) and destroy the excess peroxide by boiling before proceeding with the isolation and determination of fluoride.

9.2.5 *Vegetation*:

9.2.5.1 Reduce the gross specimen to manageable size for mixing by use of hand shears or, in the case of dried materials, a Wiley cutting mill. Take a small portion (10 to 25 g) of the mixed specimen for determination of moisture by oven drying at 80°C for 24 to 48 h.

9.2.5.2 Adjust the mass of material taken for fluoride determination according to condition of the specimen: 100 to 150 g of fresh or frozen vegetation is satisfactory, while for dried materials, such as cured hay, dried leaves, straw, and so forth, a 50-g portion is adequate.

9.2.5.3 Weigh the sample into a resistant vessel, (see 6.2). Make alkaline to phenolphthalein (see 7.7) by addition of low-fluoride CaO slurry (see 7.3), and maintain alkalinity during evaporation to dryness on a hot plate. Raise the temperature of the hot plate until charring and partial ashing have occurred. Complete the ashing at 550 to 600°C in an electric furnace reserved for the ignition of low-fluoride materials. The ash should be white or gray, indicating removal of organic matter.

9.2.5.4 When the ash has cooled, pulverize it and scrape all material from the dish; mix and determine the net mass. Store in a tightly stoppered bottle.

9.2.5.5 To effect quantitative release of fluoride combined with silica in many varieties of vegetation, fusion of the limed-ash with NaOH is required and is routinely performed on all vegetation specimens **(4-6)**. Transfer approximately 1 g of ash into a tared nickel, platinum, or Iconel crucible (see 6.1) and weigh accurately. Add about 5 g of NaOH pellets, cover the vessel, and fuse the contents for a few minutes over a gas burner. After cooling the melt, note its color; a blue-green color indicates the presence of manganese and treatment with H_2O_2 (see 7.5) is required as described in 11.7.2. Disintegrate the melt with hot water, washing down the lid and walls of the crucible. Reserve the resulting material for isolation of fluoride.

10. Isolation of Fluoride (Willard-Winter Distillation)

10.1 *Principle of Method*—The prepared sample is distilled from a strong acid such as H_2SO_4 or $HClO_4$ in the presence of a source of silica. Fluoride is steam distilled as the fluosilicic acid under conditions permitting a minimum of volatilization and entrainment of the liberating acid **(7).**

10.2 *Range and Sensitivity*—The Willard-Winter distillation method, on the macroscale, can accommodate quantities of fluoride ranging from 100 mg down to a few milligrams (mg).

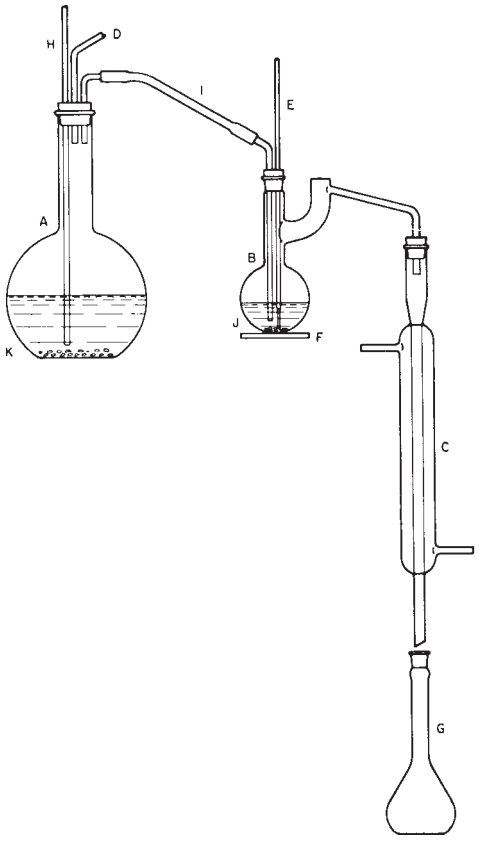
10.3 *Interferences*—Samples relatively free of interfering materials, and containing fluoride in forms from which it is easily liberated, may be subjected to a single distillation from $HClO_4$ at 135°C. Samples containing appreciable amounts of aluminum, boron, or silica require a higher temperature and larger volume of distillate for quantitative recovery. In this case, a preliminary distillation from H_2SO_4 at 165°C is commonly used (Note 1). Large amounts of chlorides are separated by precipitation with $AgClO_4$ following the first distillation. Small amounts are held back in the second distillation from $HClO_4$ by addition of $AgClO_4$ to the distillation flask. See Note 1.

NOTE 1—Generally, samples from the atmosphere do not present a problem with aluminum and silicon inhibiting the distillation of fluoride. The presence of boron in amounts sufficient to interfere with subsequent determinations of fluoride, is also unlikely. Where there is concern over these interferences, however, the distillation and analytical methods should be selected to avoid the interferences or to establish the fact that they are not significant.

10.4 *Precision and Bias*—Recovery data for the Willard-Winter distillation, as given in the literature, are difficult to dissociate from inaccuracies inherent in various methods of sample preparation and final evaluation of fluoride. Recovery data from field samples are further complicated by variability of interfering substances and ranges of fluoride contained. In general, recoveries should be within ±10 % of the amount of fluoride present. Under favorable circumstances of sample composition and fluoride range, mean recoveries of approximately 99 % with standard deviation of about 2.5 % have been reported **(7).**

10.5 *Apparatus*:

10.5.1 *Steam Generator (see* Fig. 1*A)*—2-L Florence flask made of borosilicate glass. The flask is fitted with a stopper having at least three holes for inserting 6-mm outside diameter borosilicate glass tubing. Through one of the glass tubes, bent at right angles, steam is introduced into the distilling flask. The



A–STEAM GENERATOR
B–DISTILLING FLASK
C–CONDENSER
D–STEAM RELEASE TUBE
E–THERMOMETER
F–PLATE
G–RECEIVER
H–SAFETY TUBE
I–RUBBER TUBING
J–FLINTGLASS BEAD
K–BOILING CHIPS

FIG. 1 Apparatus for Distillation of Fluoride

second tube is a steam release tube (see Fig. 1D) that controls the steam pressure. The small piece of rubber tubing that is slipped over the end of the steam release tube is clamped shut during sample distillation. The third tube is a safety tube (see Fig. 1H). If desired, other tubes may be added to permit the steam generator to supply a maximum of three distilling flasks. Any suitable heating device may be used.

10.5.2 *Distilling Flask (see* Fig. 1*B)*—A 250-mL modified Claisen flask made of borosilicate glass. The auxiliary neck of this flask is sealed and the outer end of the side tube is bent downward so that it may be attached to an upright condenser. The side tube is fitted with a one-hole rubber stopper to fit the condenser and the main neck with a two-hole stopper through which passes a thermometer and a 6-mm outside diameter heat-resistant glass inlet tube for admitting the steam. Any suitable heating device may be used.

10.5.3 *Liebig Condenser* (see Fig. 1*C*)—borosilicate glass, 300-mm jacket.

10.5.4 *Steam Release Tube* (see Fig. 1*D*)—See 11.5.1.

10.5.5 *Thermometer* (see Fig. 1*E*)—ASTM Thermometer 88C conforming to Specification E 1 will be satisfactory for this purpose.

10.5.6 *Support Plate* (see Fig. 1*F*)—Metal or ceramic.The plate shall have a perfectly round 50-mm hole in which the distilling flask is placed as shown in Fig. 1. The Claisen flask must fit well in the 50-mm hole so that the flask wall, above the liquid level, is not subjected to direct heat. Excessive heat on the wall of the flask causes the liberating acid to be distilled.

10.5.7 *Receiver* (Fig. 1G)—250- or 500-mL volumetric flask or 400-mL beaker.

10.5.8 *Safety Tube* (Fig. 1H), 6-mm outside diameter borosilicate glass, 600 mm long, one end of which is 10 mm from the bottom of the steam generator flask.

10.5.9 *Rubber Tubing* (Fig. 1I), for flask connections, made from natural rubber. Lengths of rubber tubing shall be kept as short as possible.

10.5.10 *Flint Glass Beads* (Fig. 1J), 3 mm in diameter, for use in the distilling flask to prevent superheating and to supply silica for the formation of fluosilicic acid during distillation.

10.5.11 *Porous Pumice Stones or Boiling Chips* (Fig. 1K).

10.5.12 *Pinchcock* (Fig. 1L to control steam supply from the generator.

10.6 *Reagents*:

10.6.1 *Hydrogen Peroxide Solution,* (H_2O_2) (3 %).

10.6.2 *Perchloric Acid* (70 to 72 %)—Concentrated perchloric acid ($HClO_4$, sp gr 1.66).

10.6.2.1 *Perchloric Acid* (0.05 *N*)—Dilute 4.3 mL of 70 % $HClO_4$ to 1000 mL with water.

10.6.3 *Silver Perchlorate Solution* (50 %)—Dissolve 100 g of silver perchlorate ($AgClO_4$) in 100 mL of water.

10.6.4 *Sodium Hydroxide Pellets,* (NaOH).

10.6.5 *Sulfuric Acid* (96 %)—Concentrated sulfuric acid (H_2SO_4, sp gr 1.84) (see Note 2).

NOTE 2—Acid giving excessively high fluoride blanks requires preboiling at 135°C, with admission to steam, before addition of samples.

10.7 *Procedure*:

10.7.1 *Procedure for Single Distillation, Miscellaneous Materials*:

10.7.1.1 Fill a steam generator about two thirds full of water. Add to it one NaOH pellet and a few drops of phenolphthalein indicator solution (see 7.7) to ensure that the water remains alkaline at all times. Add a piece of pumice to permit free boiling, and heat the water to boiling. Keep the steam release tube open at this time and place a pinchcock on the steam supply tubing.

10.7.1.2 Introduce the sample into a Claisen distilling flask containing five or six glass beads. Wash down the sides of the flask with water and bring the volume to 50 to 75 mL, the lesser volume being more desirable. Insert in the main neck of the flask the rubber stopper that contains the thermometer and steam inlet tube. Set the flask in the 50-mm-diameter hole in the plate and connect the outlet to a condenser.

10.7.1.3 Rinse the sides of the beaker or crucible that contained the sample with 50 mL of $HClO_4$ (70 to 72 %) (see 10.6.2) and add 1 mL of $AgClO_4$ solution (see 10.6.3). Transfer the rinsings to the distilling flask by means of a small funnel attached to the steam inlet tube. Rinse the beaker or crucible

with water and add the rinsings to the flask. Mix the contents of the flask by gentle shaking and attach the flask to the steam generator. Place a 250-mL volumetric flask under the condenser to receive the distillate and begin heating the solution in the flask. Keep the pinchcock in place on the steam inlet tube until the contents of the distilling flask reach 135°C. (**Warning—**When using $HClO_4$, the usual precautions should be taken. Hot concentrated $HClO_4$ may react explosively with reducing substances, such as organic matter. Therefore, it is wise to see that any organic matter in the sample is destroyed in the ashing process before distillation. Precautions for the use of $HClO_4$ are available in Material Safety Data Sheet Collection **(9)**.)

10.7.1.4 Remove the pinchcock on the steam inlet tube and place it on the steam release tube of the steam generator. Maintain the distillation temperature at 135 ± 2°C. Swirl the contents of the distilling flask frequently to minimize deposition on the flask wall of any siliceous residues that might retain fluoride. After collecting 250 mL of distillate during a period of about 1 h, remove the pinchcock from the steam release tube and place it on the steam inlet tube. Disconnect the rubber tubing from the steam inlet tube, and discontinue heating. (See 9.1.2.)

10.7.2 *Procedure for Single Distillation, Vegetation Ash*:

10.7.2.1 Transfer the disintegrated melt to a Claisen distilling flask (see 9.1.2), as described in 10.7.1.

10.7.2.2 Rinse the sides of the crucible in which the fusion was made with 50 mL of $HClO_4$ (70 to 72 %) (see 10.6.2) and add 1 mL of $AgClO_4$ solution (see 10.6.3).

10.7.2.3 If the sample contains manganese, add sufficient (two to ten drops) 3 % H_2O_2 solution (see 10.6.1) to the contents of the distilling flask to reduce manganese dioxide and permanganates **(10).**

10.7.2.4 Carry out the distillation as previously described, except that a 500-mL volumetric flask is used as receiver and filled with distillate during a period of about 2 h.

10.7.3 *Procedure for Double Distillation*:

10.7.3.1 Fill a steam generator, as directed in 10.7.1.1. Transfer the sample solution to a Claisen flask and rinse the sides of the beaker or crucible which contained the sample with 50 mL of concentrated H_2SO_4 (see 10.6.5). Transfer the rinsings to the distilling flask through a small funnel attached to the steam inlet tube. Mix the contents of the flask by swirling, rinse and remove the funnel, and connect the distilling flask to the steam generator. Place a 400-mL beaker under the condenser and begin heating the distilling flask and steam generator. Keep the pinchcock in place on the steam inlet tube until the contents of the distilling flask reach 165 ± 5°C. Swirl contents of the flask as required to prevent accumulation of insoluble material on the walls of the flask above the liquid level. Collect about 375 mL of distillate during a period of about 1½to 2 h.

10.7.3.2 Add NaOH (see 7.8) to the distillate until alkaline to phenolphthalein indicator (see 7.7).

10.7.3.3 Redistill the concentrated distillate from $HClO_4$ as directed in 10.7.2. Fix small quantities of chloride in the distilling flask by the addition of 1 mL of $AgClO_4$ solution (see 10.6.3). Collect a 250-mL quantity of distillate in a volumetric flask.

11. Isolation of Fluoride (Ion Exchange)

11.1 *Principle of the Method*—The sample is freed of interferences by preferential sorption on an ion exchange resin, followed by desorption of fluoride in a small volume of eluting solution. Thus, concentration of fluoride from impinger or bubbler-collection media may be achieved without the attendant danger of contamination on prolonged exposure of solutions during evaporation **(11)**.

11.2 *Range and Sensitivity*—The ion exchange procedure can be adapted to quantities of fluoride in the low-mg to µg range.

11.3 *Interferences*—Interfering cations may be eliminated by sorption of fluoride on an anion exchange resin. Fluoride is then eluted with NaOH. See Note 3.

NOTE 3—When interferences are present in cationic as well as anionic forms, both may be removed by use of a strongly basic anion exchange resin. This is accomplished by conversion of cations into strongly held complex anions, while the weakly held fluoride ions are quantitatively eluted from the column **(12)**.

11.4 *Precision and Bias*—Net recoveries for quantities of fluoride of 20 µg or more should be within ±5 % of the quantity present. Low recovery indicates incomplete preconditioning of a new column, while high recovery may be due to contamination or failure to elute completely the previous sample.

11.5 *Apparatus*:

11.5.1 *Chromatographic Column*—Dimensions of the column are not critical and many types, available from suppliers' stocks, are usable. A column made of borosilicate glass tubing 10-mm inside diameter and 160 mm long, having a fritted glass disk fused into the constricted base, and a reservoir of about 100-mL capacity at the top, is satisfactory. A short piece of poly(vinyl chloride) tubing attached to the bottom and closable with a screw hose clamp permits adjustment of flow rates and prevents complete drainage of liquid from the column.

11.5.2 *Quartz Sand, White*, −60 + 120 mesh, purified by hot extraction with 20 % NaOH (see 7.8.1) solution, followed by hot 10 % HCl (see 7.8.1) solution, is used as a protective layer at the top of the resin bed.

11.6 *Reagents*:

11.6.1 *Anion Exchange Resin Intermediate-Base* of the granular aliphatic polyamine type. Mesh size is not critical but, along with column diameter and height, is a factor in controlling flow rate of solutions. Mesh sizes of −60 + 100 or −100 + 200 are usable. (See Note 4.)

NOTE 4—Separation of fluoride may be achieved with other resins and appropriate eluting solutions; for example, Dowex 1-X8 in the acetate form may be used with elution by sodium acetate solution **(13)**.

11.6.2 *Hydrochloric Acid (HCl) Solutions*:

11.6.2.1 *HCl* (2.0 *N*)—Dilute 170 mL of conc. HCl (sp gr 1.19) to 1000 mL with water. Mix well.

11.6.2.2 *HCl* (1.0 *N*)—Dilute 85 mL of conc. HCl (sp gr 1.19) to 1000 mL with water. Mix well.

11.6.2.3 *HCl* (0.1 *N*)—Dilute 100.0 mL of 1.0 *N* HCl solution (see 11.6.2.1) to 1000 mL with water. Mix well.

11.6.2.4 *HCl* (0.01 *N*)—Dilute 100.0 mL of 0.1 *N* HCl solution (see 11.6.2.2) to 1000 mL with water. Mix well.

11.6.3 *Hydrogen Fluoride Solution* (1 ppm)—Dilute 1.0 mL of HF to 1 L with water. Mix well, and dilute 2 mL to 1 L. Store in a plastic bottle.

11.6.4 *Sodium Fluoride Solution* (1 ppm)—Dissolve 1 g of NaF in water and dilute to 1 L. Mix well and dilute 1 mL to 1 L. Store in a plastic bottle.

11.6.5 *Sodium Hydroxide* (NaOH), 2.0, 0.1, and 0.01 *N* solutions.

11.7 *Procedure*:

11.7.1 Prepare the resin column by adding a few millilitres of water to the chromatographic tube, then a slurry of resin (1 + 1) (see 11.6.1) in water. Add sufficient slurry so that when the resin has settled, a layer 100 to 120 mm in height will result. Level the resin bed by twirling the tube, and before the water level has dropped below the surface of the resin, add a 20-mm layer of quartz sand (see 11.5.2). Wash the resin with 200 mL of 2.0 *N* HCl (see 11.6.2), rinse with water; wash with 200 mL of 2.0 *N* NaOH (see 11.6.5) solution, and, finally, rinse with 200 mL water.

11.7.2 Precondition the resin by successively passing 400 mL of a solution containing 1 ppm (v) of HF (see 11.6.3) and a solution containing 1 ppm (v) of NaF (see 11.6.4) through the column at rates of about 5 mL/min. Follow this with 50 mL of 0.1 *N* NaOH solution (see 11.6.5), then 25 mL of 0.01 *N* NaOH solution (see 11.6.5). Discard the eluate. The resin is now ready for use.

11.7.2.1 *Effect of Storage*—An ion exchange column may be preserved indefinitely if the resin is covered with water. Before the column is reused, a recovery test should be made by passage of a measured quantity of standard fluoride solution through the column; 200 mL of neutral NaF solution, at a rate of 10 mL/min, is suggested. The quantity of fluoride added should approximate that expected in the sample. Fluoride is eluted, as described in 11.7, and determined by the method selected for evaluation of samples.

11.7.3 Acidify the sample solution by addition of 0.5 mL of 1 *N* HCl (see 11.6.2) per 100 mL, but add no more than 3 mL of 1 *N* HCl per sample. Remove, by filtration, any solids remaining in the sample after acidification. Pass the sample solution through the resin column at a rate of about 10 mL/min, followed by a water rinse of a few millilitres. Elute fluoride with a 25-mL portion of 0.1 *N* NaOH solution, (see 11.6.5) followed by a 25-mL portion of 0.01 *N* NaOH solution (see 11.6.5).

12. Isolation of Fluoride (Diffusion)

12.1 *Principle of Method*—An aliquot of the prepared sample is mixed with a strong acid, gently heated in a sealed container, and the liberated hydrogen fluoride is absorbed by an alkali **(14-16).**

12.2 *Range and Sensitivity*—Quantities of fluoride from about 30 µg to a few tenths of a µg may be used. In routine work, blanks range from 0.5 to 0.0 µg.

12.3 *Interferences*—Interfering materials that volatilize from acid medium must be eliminated. Sulfites are oxidized to sulfate by preliminary treatment with 30 % H_2O_2 (see 7.5) solution. Relatively large amounts of chloride may be fixed in the diffusion vessel as AgCl, by addition of 0.1 to 0.2 g of $AgClO_4$ to the sample aliquot before diffusion. Samples high in carbonates require caution upon acidification to control effervescence.

12.4 *Precision and Bias*—Recoveries from five NaF standards, covering the range from 4- to 20-µg F (five replicates of each) yielded recoveries of 97.5 to 102.5 %; average 99.4 % **(15)**. By a slightly modified technique, standards containing 0.2-, 0.5-, and 1.0-µg F (five replicates of each) yielded recoveries of 94 to 101 %; average 98.1 % **(14)**.

12.5 *Apparatus*:

12.5.1 *Microdiffusion Dish*—Disposable plastic Petri dish, 48-mm inside diameter by 8 mm deep.

12.5.2 *Oven*, thermostatically controlled, capable of maintaining temperature within ±1°C in the 50 to 60°C range.

12.5.3 *Pipet, Mohr*, capacity 0.1 mL, 0.01-mL subdivisions.

12.6 *Reagents*:

12.6.1 *Perchloric Acid*, (70 to 72 %).

12.6.2 *Silver Perchlorate, Anhydrous*, C.P. ($AgClO_4$).

12.6.3 *Sodium Hydroxide Alcoholic Solution 1 N*—Dissolve 4 g of NaOH (see 7.9) in 5 mL of water and dilute to 100 mL with ethyl-, methyl-, or Formula 30 denatured alcohol.

12.7 *Procedure*:

12.7.1 Place 0.05 mL of 1 *N* alcoholic NaOH (see 7.9) solution on the center of the inside top of the plastic Petri dish. Use the tip of the 0.1-mL Mohr pipet to spread the droplet into a circular spot of about 30 to 40 mm in diameter. Dry the top for about 1 h, under slightly reduced pressure, in a desiccator containing activated alumina.

12.7.2 Transfer a 1.0-mL aliquot of prepared sample solution to the diffusion unit. Add 2.0 mL of $HClO_4$ (see 12.6.1) and immediately close the dish with a prepared top. Place the unit in an oven maintained at the selected temperature (50 to 60°C) and allow to remain for 16 to 20 h.

12.7.3 Carefully remove the diffusion vessel from the oven and take off the top. Wash the alkaline absorbent into a 10- or 25-mL volumetric flask (a small funnel is helpful), the size of the flask depending upon amount of fluoride expected and method of measurement chosen.

13. Determination of Fluoride (Titrimetric Methods)

13.1 *Principle of Method*:

13.1.1 In the direct titration of fluoride with standard $Th(NO_3)_4$ solution, the sample solution or distillate containing sodium alizarinsulfonate is buffered at pH 3.0. Upon addition of $Th(NO_3)_4$, insoluble ThF_4 is formed. When the end point is reached, and all fluoride has reacted, the addition of another increment of $Th(NO_3)_4$ causes formation of a pink "lake" **(17).**

13.1.2 In the back titration procedure, the pink lake is first formed by addition of sodium alizarinsulfonate and a slight excess of $Th(NO_3)_4$ to the sample. Equal amounts of dye and thorium solution are added to a fluoride-free reference. The reference solution is then titrated with standard NaF solution until a color match is achieved with the unknown sample **(18)**.

13.2 *Range and Sensitivity*—The direct titration procedure can accommodate 10 to 0.05 mg of fluoride in the total sample. The back titration modifications can measure 50 to about 5 µg of fluoride in the total sample. With photometric end point detection, direct titration can also be used for the lower ranges.

13.3 *Interferences*:

13.3.1 Ions capable of forming insoluble or undissociated compounds with fluorine or with thorium interfere with these titrimetric methods and must be separated by an appropriate technique (for example, distillation, diffusion, or ion exchange). Among the more common of the interfering cations are aluminum(III), barium(II), calcium(II), iron(III), thorium(IV), titanyl(II), vanadyl(II), and zirconium(IV). The principal interfering anions are phosphate and sulfate. However, any material that constitutes an appreciable change in total ionic strength of the sample solution will affect the endpoint color as well as stoichiometry of the reaction. Thus, excessive acidity in the distillate from a Willard-Winter distillation, as from the liberating acid or chloride content of the sample, will interfere. This effect may be reduced by careful control of temperature and rate of admission of steam, and by separation of chloride. Similarly, acidity or alkalinity of eluates from ion exchange separations must be matched with that of standards used in calibration, and with the requirements of the method of evaluation.

13.3.2 Sulfide and sulfite interferences are prevented by preliminary oxidation with 30 % H_2O_2 (see 7.5) in boiling solution, as described in 10.2. Interference by free chlorine is eliminated by addition of hydroxylamine hydrochloride solution.

13.4 *Apparatus*:

13.4.1 *Fluorescent Lamp*, to provide illumination for titrating.

13.4.2 *Microburet*, having 5-mL capacity, 0.01-mL divisions, and reservoir holding about 50 mL.

13.4.3 *Nessler Tubes*—Matched set of 50-mL, tall-form tubes with shadowless bottoms. Tubes may be fitted with either ground glass or rubber stoppers. The set should be checked for optical similarity as follows: Add to the tubes 40 mL of water, 1 mL of sodium alizarinsulfonate solution (see 13.5.6), and 2 mL of 0.05 *N* HCl (see 13.5.3). Add $Th(NO_3)_4$ (see 13.5.16) solution from a buret until the color of the solution just changes to pink. Close the top of the tube and invert several times. Add the same quantity of $Th(NO_3)_4$ (see 13.5.16) solution to the remaining tubes. Fill all the tubes to the 50-mL mark with water and mix. Compare the colors and reject any tubes showing differences in the shade or intensity.

13.4.4 *Nessler Tubes*—Matched set of 100-mL, tall-form tubes with shadowless bottoms. The set should be checked for optical similarity, using the same techniques as with the 50-mL tubes, except that the quantities of reagents shall be doubled.

13.4.5 *Nessler Tube Rack or Comparator*.

13.4.6 *Photometric Titrator*—A spectrophotometer equipped with means of measuring the transmittance of the solution being titrated.

13.4.6.1 *Flow Cell*—With path length of 100 mm.

13.4.6.2 *Peristaltic Pump*—To transport the titrant from the beaker to the flow cell and back to the beaker.

13.4.6.3 An alternative method is the use of an in-situ photometer.

13.4.7 *Magnetic Stirrer*—With TFE-fluorocarbon stirring bar.

13.5 *Reagents*:

13.5.1 *Buffer-Indicator Solution*—Dissolve 0.40 g of sodium alizarin sulfonate in about 200 mL of water. Weigh 47.25 g of chloroacetic acid into a 600-mL beaker and dissolve in 200 mL of water. Add indicator solution with stirring. Dissolve 10 g NaOH in 50 mL of water, cool to approximately 15 to 20°C, and add to the above solution slowly with stirring. Filter and make to 500 mL. Prepare fresh weekly.

13.5.2 *Chloroacetate Buffer Solution*— Dissolve 9.45 g of chloroacetic acid and 2.0 g of NaOH in 100 mL of water. This solution is stable for more than two weeks if stored under refrigeration.

13.5.3 *Hydrochloric Acid, Standard* (0.05 *N*)—Dilute 4.28 mL of HCl (sp gr 1.19) to 1 L. The normality of this solution should be exactly equal to that of the (0.05 *N*) NaOH (see 13.5.13).

13.5.4 *Hydroxylamine Hydrochloride Solution (1 %)*—Add 1 g of $NH_2OH{\cdot}HCl$ to 100 mL of water.

13.5.5 *Phenolphthalein*—See 7.7.

13.5.6 *Sodium Alizarinsulfonate Solution* (0.80 g/L)—Dissolve 0.40 g of sodium alizarinsulfonate in 500 mL of water. See Note 5.

NOTE 5—In the literature, this reagent is also known as alizarin Red S, alizarin Red, alizarin-S, Alizarin carmine, alizarin, sodium alizarin sulfonate, sodium alizarin monosulfonate, monosodium alizarin sulfonate, and 2-alizarinsulfonic acid sodium salt. The dye is identified by Color Index No. 58005.

13.5.7 *Sodium Alizarinsulfonate Solution* (0.01 g/L)—Dissolve 0.01 g of sodium alizarinsulfonate in 1000 mL of water.

13.5.8 *Sodium Fluoride* (100 %) NaF.

13.5.9 *Sodium Fluoride, Standard Solution* (1 mL = 1.00-mg F^-)—Dissolve 2.2105-g NaF (see 13.5.8) in water and dilute to 1 L in a volumetric flask, mix, and transfer to a polyethylene bottle for storage.

13.5.10 *Sodium Fluoride, Standard Solution* (1 mL = 0.01-mg F^-)—Dilute 10 mL of NaF solution (1 mL = 1.00-mg F^-) (see 13.5.9) to 1 L with water in a volumetric flask, mix, and transfer to a polyethylene bottle for storage.

13.5.11 *Sodium Fluoride, Standard Solution* (1 mL = 0.1-mg F^-)—Dilute 100 mL of NaF solution (1 mL = 1.00-mg F^-) (see 13.5.9) to 1 L with water in a volumetric flask, mix, and transfer to a polyethylene bottle for storage.

13.5.12 *Sodium Hydroxide Solution* (10 g/L)—Dissolve 10 g of NaOH in water, dilute to 1 L, and mix. Store in a polyethylene bottle.

13.5.13 *Sodium Hydroxide, Standard Solution* (0.05 *N*)—Dissolve 2.00 g of NaOH (see 13.5.3) in water and dilute to 1 L. The normality of this solution should be exactly equal to that of the standard HCl (0.05 *N*) (see 13.5.3). Store in a polyethylene bottle.

13.5.14 *Thorium Nitrate, Standard Stock Solution* (1 mL = 1.9-mg F^-)—Dissolve 13.80 g of thorium nitrate tetrahydrate [$Th(NO_3)_4 \cdot 4H_2O$] in water and dilute to 1 L and mix. Store in a polyethylene bottle.

13.5.15 *Thorium Nitrate Solution* (0.25 g/L)—Dissolve 0.25 g of thorium nitrate tetrahydrate [$Th(NO_3)_4 \cdot 4H_2O$] in water, dilute to 1 L, and mix. Store in a polyethylene bottle.

13.5.16 *Thorium Nitrate Solution,* 0.01 *N* (0.19-g F^-/L)—Dilute a 100-mL aliquot of the stock solution (see 13.5.14) to 1 L and store in a polyethylene bottle.

13.5.17 *Effects of Storage*—All reagent solutions listed are stable at room temperature except as individually noted.

13.6 *Procedure*:

13.6.1 *Procedure for Direct Titration, High Concentration (10- to 0.05-mg F^- in Total Sample)* :

13.6.1.1 Pipet an aliquot of the distillate into a 400-mL beaker and dilute to 100 mL with water. Add 1 mL of sodium alizarinsulfonate solution (0.80 g/L) (see 13.5.6) and then NaOH (10 g/L) (see 7.8) dropwise until a pink color is obtained. Discharge the pink color by adding 0.05 *N* HCl (see 13.5.3) dropwise. Add 1 mL of chloroacetate buffer solution (see 13.5.2) dropwise and titrate with $Th(NO_3)_4$ (1 mL = 1.9-mg F^-) (see 13.5.14) to a faint, persistent, pink end point. Determine a blank obtained by carrying the same amount of all reagents through the entire procedure.

13.6.2 *Procedure for Back Titration, Medium Concentration (0.05- to 0.01-mg F^- in Total Sample)*:

13.6.2.1 Transfer 50 mL of the distillate into a 50-mL Nessler tube and add 1 mL of sodium alizarinsulfonate solution (0.01 g/L) (see 13.5.7) and sufficient 0.05 *N* NaOH (see 13.5.13) solution to produce a pink color. Note precisely the volume of 0.05 *N* NaOH solution required for neutralization; then discard the titrated solution. If more than 4 mL of 0.05 *N* NaOH is required, make the remaining distillate alkaline to phenolphthalein (see 7.7), evaporate to 10 to 15 mL, and transfer it to a distilling flask. Repeat the distillation, precautions being taken to reduce the amount of $HClO_4$ distilled over.

13.6.2.2 Transfer another 50-mL portion of distillate into a 50-mL Nessler tube (sample tube) and add 1 mL of sodium alizarinsulfonate solution (0.01 g/L) (see 13.5.7). Adjust the acidity with 0.05 *N* HCl (see 13.5.3) until the equivalent of exactly 2 mL of acid is present; that is, 2 mL minus the volume in mL of 0.05 *N* NaOH (see 13.5.3) solution required for neutralization as described. If between 2 and 4 mL of 0.05 *N* NaOH (see 13.5.3) solution were required for neutralization, omit the addition of HCl to the distillate. Add $Th(NO_3)_4$ (25 g/L) (see 13.5.15) from a microburet until a faint pink color appears. Note the volume of $Th(NO_3)_4$ solution required, and save the Nessler tube for comparison with the standard.

13.6.2.3 Pour 50 mL of water into a 50-mL Nessler tube (standard tube) and add 1 mL of sodium alizarinsulfonate solution of 0.01 g/L (see 13.5.7). If neutralization of the sample requires 2 mL or less of 0.05 *N* NaOH (see 13.5.13) solution, pipet exactly 2 mL of 0.05 *N* HCl (see 13.5.3) into the standard tube. If the 50-mL aliquot of the distillate requires more than 2 mL of 0.05 *N* NaOH solution (see 13.5.13) for neutralization, no further acidification of the distillate is necessary, but add to the standard tube a quantity of acid equivalent to that found in the sample distillate.

13.6.2.4 From a microburet add NaF (see 13.5.11) solution (1 mL = 0.01-mg F^-) equivalent to about 80 % of the fluoride present in the sample aliquot, as indicated by the $Th(NO_3)_4$ solution required. Mix thoroughly, add the same volume of $Th(NO_3)_4$ solution as that required for titration of the sample aliquot as described, and again mix thoroughly. The color in the standard tube will be deeper than that in the sample tube.

13.6.2.5 From the microburet continue to add NaF solution (1 mL = 0.1-mg F^-) (see 13.5.10) to the standard tube until its color matches that of the sample tube. (If the colors cannot be matched, repeat the distillation.) Equalize the volumes in the sample and standard tubes by adding water. After the addition of water, mix thoroughly, then allow all bubbles to escape before making the final color comparison. Check the end point by adding one or two drops of NaF solution (1 mL = 0.01-mg F^-) (see 13.5.11) to the standard tube. If the colors were originally matched, the color in the standard tube will be distinctly lighter in shade than that in the sample tube.

13.6.2.6 Determine a blank by carrying the same amount of all reagents through the procedure described. With proper attention to details, blanks of 5 µg of fluoride, or less, can be obtained.

13.6.3 *Procedure for Back Titration, Low Concentrations (Less Than 0.01-mg F^- in Total Sample)*—Distill successive 85- to 90-mL portions of distillate directly into three or four 100-mL Nessler tubes. Take care to keep the amount of $HClO_4$ distilling over as small as possible, because the entire distillate is titrated and there is no aliquot available for a separate acidity determination. Analyze each of the distillate portions in the 100-mL Nessler tubes separately as follows:

13.6.3.1 Add 2 mL of sodium alizarinsulfonate solution (0.01 g/L) (see 13.5.7) and neutralize the acid by adding 0.05 *N* NaOH solution (see 13.5.13) until a pink color is produced. Add 4 mL of 0.05 *N* HCl (see 13.5.3) and sufficient $Th(NO_3)_4$ (see 13.5.15) to provide a faint pink color. Compare the treated distillate portion with a standard of equal total volume containing 2 mL of sodium alizarinsulfonate solution (0.01 g/L) (see 13.5.7), 4 mL of HCl (see 13.5.3), and the same volume of $Th(NO_3)_4$ (see 13.5.15) as is required to produce the pink color in the sample tube. Add NaF (see 13.5.11) solution to the standard tube until the color matches that of the sample tube. The sum of all significant amounts of fluoride found in each successive portion of distillate is the total amount of fluoride in the sample.

13.6.4 *Procedure for Photometric Titration*:

13.6.4.1 Transfer the distillate to a beaker and add 5 mL of hydroxylamine hydrochloride solution (see 13.5.4). Adjust, if necessary, to pH 3.6 with 0.05 *N* $HClO_4$ (see 10.6.2.1) and then add 5 mL of buffer-indicator solution (see 13.5.1) (see Note 6).

NOTE 6—The addition of buffer-indicator solution should adjust the pH to 3.0. For amounts of fluoride ordinarily encountered, the pH of the distillate should be 3.5 to 3.7 if the distillation is properly controlled. The addition of buffer-indicator solution will maintain a pH of 3.0 under these conditions. For extreme cases, where pH of the distillate is less than 3.5, use 0.05 *N* NaOH (see 13.5.13) to raise the pH to the proper level. However, it has been found to be the rule that distillations properly

conducted will have a pH greater than 3.5. The use of NaOH for neutralization produces a slight change in the factor because of the $NaClO_4$ formed.

13.6.4.2 Using the peristaltic pump (see 13.4.6.2), pump the distillate through the flow-through cell (see 13.4.6.1) in the spectrophotometer (see 13.4.6), and back into the beaker. Start the stirring motor (see 13.4.7). Adjust the spectrophotometer wavelength to 525 nm, and adjust the spectrophotometer to give a transmittance reading of 100.

13.6.4.3 Titrate with standard $Th(NO_3)_4$ (see 13.5.16) (0.01 *N* solution) to a transmittance reading of 86.7 %. Record the volume to the nearest 0.005 mL.

13.6.4.4 Deduct a blank obtained by carrying the same amount of all reagents through the entire procedure, including the preliminary distillation and titration steps. Determine the amount of fluoride present from the calibration chart.

13.7 *Calibration and Standards*:

13.7.1 *$Th(NO_3)_4$, Standard Stock Solution* (1 mL = 1.9-mg F^-)—Standardize this solution as follows:

13.7.1.1 Weigh 0.100 g of NaF (see 13.5.8) into a distilling flask and collect 250 mL of distillate as previously described. Titrate 50 mL of the distillate (20 mg of NaF) with the solution being standardized. Carry a blank through the same procedure. Calculate the concentration of the $Th(NO_3)_4$ as follows:

$$X = (C \times 20)/(A - B) \quad (1)$$

where:

X = concentration, mg/ml of F,
A = volume of $Th(NO_3)_4 \cdot 4\ H_2O$ solution required for titration of the fluoride, mL,
B = volume of $Th(NO_3)_4 \cdot 4\ H_2O$ solution required for titration of the blank, mL, and
C = 0.4524 when titrating NaF.

13.7.2 *Thorium Nitrate Solution* (0.01 *N*) (0.19-g F^-/L)—Prepare a calibration curve for this solution from data obtained in the following way:

13.7.2.1 Pipet aliquots of standard NaF (see 13.5.10) solution covering the range 10 to 1000 µg of fluoride into 500-mL volumetric flasks and dilute to volume. Transfer to a beaker, add 5 mL of hydroxylamine hydrochloride solution (see 13.5.4), and adjust to pH 3.6 with 0.05 *N* $HClO_4$ (see 10.6.2.1). Add 5 mL of buffer-indicator solution (see 13.5.1) and titrate as described in 13.6.4.

13.8 *Calculation*:

13.8.1 Calculate the fluoride ion content of the total distillate (Note 7) as follows:

$$F = [(A - B)\ CD]/E \quad (2)$$

where:

F = mass of fluoride ion in total distillate, mg,
A = volume of titrating solution (see Note 8) used in titration of sample aliquot, mL,
B = volume of titrating solution (see Note 8) used in titration of sample aliquot, mL,
C = fluoride equivalent of titrating solution (see Note 8), mg/mL of F,
D = volume of total distillate collected (see Note 7), mL, and
E = volume of distillate titrated (see Note 7), mL.

NOTE 7—The volume of total distillate collected normally is 250 mL. However, if any other volume of total distillate is collected, this volume shall be substituted for 250. The volume of the distillate titrated normally is 50 mL but may vary as described in 13.6.3. If this procedure applies, for each portion of distillate titrated, the value of E is equal to the value of D.

NOTE 8—The term "titrating solution" refers to either the $Th(NO_3)_4$ solution used in accordance with 13.6.1 or the NaF solution (1 mL = 0.01 mg F^-) used in 13.6.2 and 13.6.3.

13.8.2 Calculate the fluoride concentration in the atmosphere at 25°C and 101.3 kPa, in terms of ppm (v) of HF or fluorine (F_2), or mg of particulate fluoride/^{3}, as follows:

$$\text{HF, ppm (v)} = [438 \times F \times (273 + t)]/PV \quad (3)$$

$$F_2\text{, ppm (v)} = [219 \times F \times (273 + t)]/PV \quad (4)$$

$$\text{Particulate fluoride, mg/m}^3 = [340 \times F \times (273 + t)]/PV \quad (5)$$

where:

F = mass of fluoride ion in total sample, mg,
P = sampling pressure in kPa (mm Hg),
t = sampling temperature, °C, and
V = sample volume, L.

13.8.3 Calculate the fluoride concentration in vegetation on the oven-dry basis, as follows:

$$\text{Fluoride, ppm (v) (dry basis)} = \frac{F \times A \times 1000}{W \times S \times [1 - (M/100)]} \quad (6)$$

where:

X = fluoride concentration (on the oven−dried basis), ppm (v),
F = mass of fluoride ion in total distillate, mg,
A = mass of total ash, g,
W = mass of ash distilled, g, and
S = mass of fresh sample, g.

13.9 *Precision and Bias*—Precision and bias are essentially functions of the fluoride isolation technique.

14. Determination of Fluoride (Spectrophotometric Methods)

14.1 *Principle of Method*—Reaction of fluoride with the metal ion moiety of a metal-dye complex results in fading [Zirconium-Eriochrome Cyanine R and Zirconium-SPADNS reagents] or increase [Lanthanum-Alizarin Fluorine Blue] in the absorbance of the solution **(19-21)**.

14.2 *Sensitivity and Range*:

14.2.1 Both Zirconium-Eriochrome Cyanine R and Zirconium-SPADNS reagents obey Beer's law over the range from 0 to 1.40 µg/mL of F^- with a detection limit of the order of 0.02 µg/mL of F^-. The procedure given for the lower-range, Lanthanum-Alizarin Fluorine Blue, covers the range from 0 to 0.5 µg/mL of F^- with a detection limit of approximately 0.015 µg/mL.

14.2.2 In common with other spectrophotometric methods, these are temperature-sensitive and absorbances must be read within ±2°C of the temperature at which the respective calibration curve was established.

14.3 *Interferences*:

14.3.1 Moderate variations in acidity of sample solutions will not interfere with the Zirconium-Eriochrome Cyanine R or Zirconium-SPADNS reagents. The Lanthanum-Alizarin Fluorine Blue reagent has greater pH sensitivity, and solutions must

not exceed the capacity of the buffer system to maintain an apparent pH 4.50 ± 0.02.

14.3.2 Many ions interfere with these fluoride reagents, but those most likely to be encountered in analysis of ambient air are aluminum, iron, phosphate, and sulfate. If these are present above the trace level, their effects must be eliminated. Distillation, diffusion, or ion exchange shall be used but, in certain cases, complexation-extraction may be advantageous **(22).**

14.3.3 In vegetation analysis, ashing and distillation by the Willard-Winter technique generally assure a sample solution sufficiently free of interfering ions for direct colorimetric evaluation. Traces of free chlorine in the distillate, if present, must be reduced with hydroxylamine hydrochloride.

14.4 *Precision and Bias*—Because of the wide variability in composition of samples, and in methods and conditions of sampling, no general statements of precision and accuracy for field samples can be given. Precision studies of pure NaF standards indicate that, within the concentration ranges for which the reagents follow Beer's law, standard deviation of ±0.015 to 0.020 µg/mL of F should be expected.

14.5 *Apparatus*:

14.5.1 *Spectrophotometer*—An instrument capable of accepting sample cells of 10- to 25-mm optical path, and that is adjustable throughout the visible wavelength region, is required. Each spectrophotometer sample cell is given an identification mark and calibrated by reading a portion of the same reagent blank solution at the designated wavelength. The determined cell correction is subsequently applied to all absorbance readings made in that cell.

14.6 *Reagents*:

14.6.1 *Acetic Acid (Glacial),* (sp gr 1.06).

14.6.2 *Acetone* (Reagent grade).

14.6.3 *Alizarin Fluorine Blue (Alizarin Complexone)*—3-amino-ethylalizarin-N-N diacetic acid.

14.6.4 *Ammonium Acetate Solution* (20 %)—Dissolve 20.0 g of ammonium acetate in water and dilute to 100 mL.

14.6.5 *Ammonium Hydroxide* (sp gr 0.880) (NH_4OH).

14.6.6 *Eriochrome Cyanine R Solution*—Dissolve 1.800 g of Eriochrome Cyanine R (Mordant Blue 3, Color Index No. 43820) in water to make 1 L. Solution is stable for more than a year when protected from light.

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

14.6.8 *Hydrochloric Acid* (2 *N*)—Dilute 171 mL of concentrated HCl to 1 L.

14.6.9 *Lanthanum Chloride* (99.9 % Assay) $LaCl_3$.

14.6.10 *Lanthanum-Alizarin Fluorine Blue*—Dissolve 8.2 g of sodium acetate (see 14.6.11) in 6 mL of glacial acetic acid (see 14.6.1), and sufficient water to permit solution, and transfer to a 200-mL volumetric flask. Dissolve 0.0479 g of alizarin fluorine blue (see 14.6.3) in 1.0 mL of 20 % ammonium acetate solution (see 14.6.4), 0.1 mL of NH_4OH (see 14.6.5), and 5 mL of water. Filter this solution[8] into the 200-mL volumetric flask. Wash the filter with a few drops of water and discard the residue. Add 100 mL of acetone (see 14.6.2), slowly and with mixing, to the flask. Dissolve separately 0.612 g of $LaCl_3$ (see 14.6.9), in 2.5 mL of 2 *N* HCl (see 14.6.8), warming slightly to promote solution, and combine this with the flask contents. Dilute, mix well, cool the solution to room temperature, and adjust the volume to the mark. The reagent solution is stable for about one week if kept under refrigeration. See Note 9.

NOTE 9—An equimolar concentration of $La(NO_3)_3$ may be substituted for the chloride.

14.6.11 *Sodium Acetate*:

14.6.12 *Sodium Fluoride, Stock Solution* (1 mL = 1.0-mg F^-)—Dissolve 2.2105 g of NaF in water and dilute to 1 L. Store in a polyethylene bottle.

14.6.13 *Sodium Fluoride, Working Standard Solution* (1 mL = 10-µg F^-)—Dilute 5.0 mL of the stock solution (see 14.6.12) to 500 mL. Store in a polyethylene bottle.

14.6.14 *SPADNS Solution* (4,5-dihydroxy3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt). Dissolve 0.985-g SPADNS dye in water and dilute to 500 mL.

14.6.15 *SPADNS, Reference Solution*—Add 10 mL of SPADNS solution (see 14.6.14) to 100 mL of water and acidify with a solution prepared by diluting 7 mL of concentrated HCl (see 14.6.7) to 10 mL. This solution may be stored and reused repeatedly.

14.6.16 *Zirconium Solution*—Dissolve 0.265 g of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in 50 mL of water, add 700 mL of concentrated HCl (see 14.6.7), and dilute to 1 L with water.

14.6.17 *Zirconium-Eriochrome Cyanine R Reagent*—Mix equal volumes of the Eriochrome Cyanine R (see 14.6.6) and the zirconium solutions (see 14.6.16). Cool to room temperature before use. Prepare fresh daily.

14.6.18 *Zirconium-SPADNS Reagent*—Mix equal volumes of the SPADNS (see 14.6.14) and the zirconium (see 14.6.16) solutions. Cool to room temperature before use. This reagent may be stored for several months, at room temperature, in a polyethylene bottle.

14.6.19 *Effects of Storage*—Reagents used in these procedures are stable, except as individually noted.

14.7 *Procedure*:

14.7.1 *Procedure for Intermediate Range: Zirconium-Eriochrome Cyanine R Reagent*—Transfer an aliquot of the prepared sample, standard, or blank solution to a 25-mL volumetric flask containing 4 mL of the Zirconium-Eriochrome Cyanine R Reagent (see 14.6.17). Dilute the solution to the mark, mix well, and allow to stand for 30 min for temperature equilibration. Transfer the solution to a calibrated spectrophotometer cell of about 25-mm light path. The spectrophotometer is set on a wavelength of 536 nm and the light control adjusted to an absorbance value of 0.500 on a reagent blank similarly prepared.

14.7.1.1 Spectrophotometer cells of 10-mm light path may be used by making the following adjustments of volumes: transfer the aliquot of sample, standard, or blank solution to a 10-mL volumetric flask and add 3 mL of Zirconium-Eriochrome Cyanine R Reagent (see 14.6.17). Dilute the mixture to the mark, mix well, and allow to stand for 30 min; then read absorbance as previously described.

[8] Use fast filter paper or equivalent.

14.7.1.2 *Procedure for Intermediate Range: Zirconium-SPADNS Reagent*—Dilute a suitable aliquot of the sample solution to 25 mL and add 5.0 mL of Zirconium-SPADNS Reagent (see 14.6.18). Mix and allow to stand for 30 min to establish temperature equilibrium before transferring the solution to a spectrophotometer cell (cells of 10- to 25-mm optical path may be used). Measure the absorbance value at 570 nm with the spectrophotometer adjusted to read zero absorbance on the SPADNS Reference Solution (see 14.6.15).

14.7.2 *Procedure, Lower Range—Lanthanum-Alizarin Fluorine Blue Reagent*—Transfer of a suitable aliquot of sample solution, containing no more than 4 µg of fluoride, to a 10-mL volumetric flask. Add 3 mL of Lanthanum-Alizarin Fluorine Blue Reagent (see 14.6.10), dilute to the mark, and mix well. Allow to stand for 30 min. Measure the absorbance at 622 nm, in a calibrated 10-mm cell, using a reagent blank as reference.

14.8 *Calibration and Standards*:

14.8.1 *Zirconium-Eriochrome Cyanine R Reagent*—Prepare a standard series, spanning the range of 0 to 20 µg of fluoride (see 14.6.13), by pipeting aliquots of the standard NaF solution (10 µg/mL of F^-) into 25-mL volumetric flasks. Add 4 mL of Zirconium-Eriochrome Cyanine R Reagent (see 14.6.17) to each flask, dilute to the mark, and mix thoroughly. Allow the standards to stand until solution temperature has equilibrated at the desired value. Measure absorbances at 536 nm, in 25-mm cells, against a reagent blank for which the spectrophotometer is adjusted to read 0.500 absorbance unit. Plot a calibration curve relating fluoride concentration, in µg, to absorbance values at the selected working temperature using regression analysis by the method of least squares.

14.8.1.1 If 10-mm cells are to be used, a similar standard series is prepared in 10-mL volumetric flasks, adding 3-mL Zirconium-Eriochrome Cyanine R Reagent (see 14.6.17) to each flask, and reading as described above.

14.8.2 *Zirconium-SPADNS Reagent*—Prepare a standard series containing from 0 to 35 µg of fluoride by pipeting aliquots of the standard NaF solution (10 µg/mL of F^-) (see 14.6.13) into 25-mL volumetric flasks. Add 5 mL of Zirconium-SPADNS Reagent (see 14.6.18) to each flask, dilute to the mark, and mix well. Allow the standards to stand 30 min to reach temperature equilibrium at the desired value. Measure absorbances at 570 nm after zeroing the spectrophotometer on the SPADNS Reference Solution (see 14.6.15). Prepare a calibration curve relating fluoride concentration, in µg, to absorbance values at the selected working temperature using regression analysis by the method of least squares.

14.8.3 *Lanthanum-Alizarin Fluorine Reagent*—Prepare a standard series containing 0 to 4 µg of fluoride by measuring portions of the standard NaF solution (10 µg/mL of F^-) (see 14.6.13) into 10-mL volumetric flasks. Add 3 mL of Lanthanum-Alizarin Fluorine Blue Reagent (see 14.6.10) to each flask, dilute to the mark, mix, and let stand for 30 min at the selected temperature. Measure the absorbances at 622 nm in 10-mm cells, using a reagent blank as reference.

14.9 *Calculation*—Concentrations of fluoride in air or vegetation samples are calculated by use of the formulas given in 13.8.1-13.8.3.

15. Determination of Fluoride (Potentiometric Method)

15.1 *Scope*:

15.1.1 This method can be used for the determination of inorganic fluorides in aqueous solution obtained from impingers, bubblers, impregnated filter papers, coated tubes, or other air sampling devices or plant tissues **(23,24).**

15.1.2 It uses a simple extraction followed by direct analysis with the fluoride specific-ion electrode and electrometer **(25)**. The results are comparable to those obtained by high temperature ashing and alkaline fusion, with subsequent release of fluorine by microdistillation, followed by colorimetric or potentiometric analysis.

15.1.3 The range of measurement of the electrode is 0.019 to 19 000 µg/mL of F^- of solution (10^{-6} to 1 *M*), **(26)**; however, the recommended range of analysis for air samples is between 0.03 and 10 µg/mL of F^- in solution. Slow response time and nonlinearity of the calibration curve cause measurements below 0.1 µg/mL of F^- to be less desirable. Consequently, the minimum concentration of fluoride in the atmosphere that can be measured in the recommended range is 1 µg/m^3 of F^- if the air sample volume is 10 m^3 and the total sample is collected in 50 mL of solution.

15.2 *Summary of Method*:

15.2.1 Plant tissue is prepared by being dried in a forced-draft oven and being ground to a uniform size. It is weighed into a plastic tube, a solution of $HClO_4$ is added, and the mixture is heated and shaken.

15.2.1.1 The fluoride content of the solution is measured directly in the tube by insertion of the specific-ion electrode into the stirred solution and reading the output of the electrometer.

15.2.2 Record the potential in millivolts (mV) and convert to µg/mL of F^- using a calibration curve.

15.3 *Significance*:

15.3.1 This method provides a rapid and simple means of measuring the inorganic fluoride content of ambient air samples.

15.3.2 Potentiometric analysis, by means of the fluoride ion electrode, can be automated if a great many samples must be analyzed daily.

15.3.3 The method is particularly well suited to analysis of liquids from impregnated filter paper (see Test Method D 3267) and bicarbonate-coated tube collection (see Method D 3268) since fluoride obtained from these sampling methods is contained in small volumes of solution. It is not as well suited to measurement of low atmospheric concentrations of fluoride collected in impingers or bubblers because the large volume of liquid may yield fluoride concentrations below the most suitable range of measurement.

15.4 *Interferences*:

15.4.1 The electrode measures the free fluoride ion (fluoride activity); therefore, any substances that complex the fluoride or conditions that reduce the dissociation of fluoride will produce errors. Any substance that coats or reacts with the electrode crystal or otherwise slows the response time to fluoride will produce analytical errors. Hydroxyl ions are measured by the electrode when the OH^- to F^- concentration ratio is in excess of ten to one. A high concentration of dissolved salts depresses

fluoride ion activity; therefore, differences in total ionic strength between samples and standard fluoride solutions can be a source of error.

15.4.1.1 There was no significant change in electrode response when standard 1 ppm by mass solutions of fluoride were amended with 4 ppm by mass of Copper II, Nickel II, Zinc II, Cadmium II, Lead II, Iron II, Manganese II, or Aluminum III. However, solutions containing Aluminum III changed after standing overnight.

15.5 *Apparatus*:

15.5.1 A combination fluoride ion electrode or separate fluoride ion and reference electrodes.

15.5.2 An electrometer or an expanded scale pH meter with a millivolt scale for measurement of potential.

15.5.3 A compatible recorder can be attached to the electrometer for obtaining a permanent record of analytical results.

15.5.4 Polytetrafluoroethylene-coated magnetic stirring bars and air-driven magnetic stirrers. The latter device avoids the heating effect of motor-driven stirrers.

15.5.5 *Repeating Dispenser*—25-mL capacity.

15.5.6 *Polypropylene Tubes*—50-mL capacity, graduated.

15.5.7 *Water Bath*—With shaker.

15.5.8 *Tube Rack*—Epoxy-coated.

15.5.9 *Mechanical Convection Oven*.

15.6 *Reagents*:

15.6.1 *Perchloric Acid* (0.1 *N*)—Dilute 8.6 mL of 70 % $HClO_4$, sp gr 1.66, to 1 L with water.

15.6.2 *Stock Solution*—100 µg/mL of F^-. Dissolve 0.222 g of dry NaF in water and dilute to 1 L. Store in a plastic bottle in the cold and allow to come to room temperature before use.

15.6.3 *Standard Fluoride Solution*, 0.2 µg/mL of F^-. Take 2.0 mL of stock solution (see 15.6.2) (100 µg of F^-/mL), add 8.6 mL of 70 % $HClO_4$, and dilute to 1 L with water.

15.6.4 *Standard Fluoride Solution*, 1.0 µg/mL of F^-. Take 10.0 mL of stock solution (see 15.6.2) (100-µg/mL F), add 8.6 mL of 70 % $HClO_4$, and dilute to 1 L with water.

15.6.5 *Standard Fluoride Solution*, 5.0 µg/mL of F^-. Take 50 mL of stock solution (see 15.6.2) (100-µg/mL F^-), add 8.6 mL of 70 % $HClO_4$, and dilute to 1 L with water.

15.6.6 *Plant Tissue Wash Solution*—Dissolve 0.5 g of detergent and 0.5 g of sodium(Tetra)ethylenediamine tetraacetate (Na_4EDTA) in water to make 1 L.

15.7 For calibration of the electrodes and electrometer, follow the instruction manual **(27)** using 0.2, 1.0, and 5.0 µg/mL of F^- solutions in the concentration mode. The calibration assumes Nerstian response of the electrode and a sample temperature of 20°C.

15.7.1 The error in not correcting to 25°C is not significant.

15.8 *Effects of Storage*:

15.8.1 If sample solutions are to be stored even for a few hours before analysis, they should be held in plastic rather than glass containers.

15.8.2 For overnight storage, place the electrode in a solution containing 1 µg/mL of F and no salts or buffer. For long periods of storage, the electrode may be kept dry after rinsing the exterior with distilled water.

15.9 *Procedure*:

15.9.1 If the plant tissue is to be washed, place fresh tissue in a cheesecloth square, fold the ends up, and wash in a polyethylene container with the plant tissue wash solution for 30 s with gentle agitation.

15.9.1.1 Remove the cheesecloth containing the tissue and allow to drain for a few seconds, then rinse for 10 s in each of three containers of water. Blot dry in paper towels to remove excess water.

15.9.1.2 Place the tissue in a labeled Kraft paper bag and dry in a mechanical convection oven at 80°C for 24 h.

15.9.1.3 Grind dried tissue in a Wiley mill to pass a 425-µm mesh sieve. Collect the sieved material in a labelled polyethylene container with a moisture-proof seal.

15.9.2 Weigh 0.5 g of well-mixed sample into a polypropylene tube and add 25 mL of 0.1 *N* $HClO_4$ (see 15.6.1). Close the tube securely with a screw cap and place in a test tube rack.

15.9.2.1 Prepare up to three racks of tubes in this manner containing samples, two controls, and two blanks.

15.9.2.2 Place the racks in the water bath and shake at 80°C for 4 h.

15.9.2.3 Add an additional 25 mL of 0.1 *N* $HClO_4$ (see 15.6.1) to each of the tubes.

15.9.2.4 Add a tapered tip magnetic stirring bar to each tube and place on the magnetic stirrer.

15.9.2.5 Lower the specific-ion probe into the solution. Stir thoroughly and record the reading after it has stabilized to within ±1 digit.

15.10 *Precautions*:

15.10.1 Proper electrode response is essential to accurate measurements. Nonlinearity of the calibration curve (as determined by linear regression using the method of least squares), poor reproducibility of replicate analysis (more than two standard deviations) or slow response time (in excess of 2 min) are indications that the electrode may not be operating properly.

15.10.1.1 Check the electrometer by substituting a pH electrode for the fluoride electrode. If pH measurements (on the expanded scale) are satisfactory, faulty operation of the fluoride electrode is indicated.

15.10.2 If response of the electrode is slow, drain or replace the reference solution in the reference electrode or the combination electrode.

15.10.2.1 If operation is not improved, the end of the fluoride electrode can be dipped briefly into absolute methanol followed by 0.1 *N* HCl. After rinsing with deionized water, the electrode is ready for use.

15.10.2.2 This procedure should be used infrequently to avoid an effect of solvents on the plastic housing of the electrode.

15.11 *Calculation of Results*—Concentration of fluoride in the solution is read from the calibration curve in µg/mL using millivolt values given by analysis. Determine the final atmospheric fluoride concentration by calculating total mass of fluoride in the original air sample and dividing by the total volume of air sampled as indicated by the following equation:

$$X = F \times V/A \quad (7)$$

where:

X = concentration of fluoride, µg/m^3,
F = fluoride concentration found in µg/mL,
V = volume of sample solution, mL, and
A = volume of air samples in m^3 at 101.3 kPa and 25°C.

15.12 *Precision and Bias*:

15.12.1 The results from 75 replicates of a standard sample produced a relative standard deviation of 4.13 % **(25)**.

15.12.2 Corresponding values obtained by the method of standard addition to the same sample solutions produced a standard deviation of 5.29 %.

15.12.3 The mean recovery from 28 different samples when compared to the Test Methods D 3270 procedure produced a mean of 99.6 % with a standard deviation of 5.57 %.

16. Keywords

16.1 ambient atmospheres; fluoride, colorimetric determination of; fluoride, potentiometric determination of; fluoride, titrimetric determination of

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