TRANSMITTAL OF RULES ADOPTED

FROM: WASHINGTON STATE AIR POLLUTION CONTROL BOARD
(Name of Agency)

TO: CODE REVISER
LEGISLATIVE BLDG (Southwest Corner, Ground Floor)
Olympia 98501

The enclosed Permanent rules [x] Emergency rules [ ], being order No. 15

relating to (Name of rules or description of subject matter)

chapter 18-48 WAC establishing standards for the fluoride content of forage and standards for the gaseous fluorides in the ambient air. This chapter also provides for a monitoring program, sampling and analysis.

(ALTERNATIVE A. Use only for adoption of permanent rules)

pursuant to Notice No. 2642① filed with the code reviser on 4-30-70② (date) were regularly adopted as permanent rules of this agency at Seattle, Washington (place) on 5-20-70 (date) and are herewith filed in the office of the code reviser pursuant to chapter 34.04 RCW. The effective date of such rules shall be _____.③

(ALTERNATIVE B. Use only for adoption of emergency rules)

pursuant to its finding that the immediate adoption of these rules is necessary for the preservation of the public health, safety, or general welfare and that observance of the requirements of notice and opportunity to present views on the proposed action would be contrary to the public interest, were regularly adopted as emergency rules of this agency at _____ (place) on _____ (date) and are herewith filed in the office of the code reviser pursuant to chapter 34.04 RCW.

Dated this 20th day of May 1970.

STATE OF WASHINGTON
FILED
MAY 28 1970
CODE REVISER'S OFFICE
KET # 2189 FILE #

WASHINGTON STATE AIR POLLUTION CONTROL BOARD
(AGENCY)

By Wallace Lane, M. D.

Chairman
Title

① NOTICE NUMBER AS APPEARS ON THE COPY OF NOTICE RETURNED TO YOU BY REVISER'S OFFICE (IF PROCEEDINGS WERE CONTINUED, USE NO. OF LAST NOTICE)
② STAMPED DATE AS APPEARS ON THE COPY OF NOTICE RETURNED TO YOU BY REVISER'S OFFICE (IF PROCEEDINGS WERE CONTINUED, USE DATE OF LAST NOTICE)
③ UNLESS A LATER DATE IS SPECIFIED IN THIS ORDER OR IS PRESCRIBED IN ANOTHER STATUTE, RULES ARE EFFECTIVE 30 DAYS AFTER FILING: RCW 34.04.040. LEAVE THIS SPACE BLANK EXCEPT IN SUCH SPECIAL CASES.

Form Adopted 12/11/67, Effective 1/17/68 (Form CR-2)

STATE OF WASHINGTON

STATE AIR POLLUTION CONTROL BOARD

PURSUANT to the authority vested in it by the laws of the state of Washington, particularly chapter 70.94 RCW, and pursuant to chapter 34.04 RCW:

THE STATE AIR POLLUTION CONTROL BOARD DOES HEREBY ADOPT as permanent rules and regulations chapter 18-48 WAC pertaining to fluorides. These rules and regulations, as attached hereto, establish two standards, one for the fluoride content of forage and the other for the gaseous fluorides in the ambient air, and establish compliance with the standards, sampling and analysis.

THIS order, after being first recorded in the order register of this agency, shall be forwarded to the Code Reviser for filing pursuant to chapter 34.04 RCW and chapter 1-12 WAC.

DONE in the City of Seattle, County of King, State of Washington, this twentieth day of May, 1970.

WASHINGTON STATE AIR POLLUTION CONTROL BOARD

Wallace Lane, M.D., Chairman

Donald W. Moos

August T. Rossano

Gordon Tongue

John C. Ranger

Harvey S. Poll

Frank Roberts

Glen A. Yake

Harold V. Schubert

CHAPTER 18-48

FLUORIDES

WAC 18-48-010 POLICY LIMITATIONS. The standards set forth within these regulations are intended to protect livestock and vegetation. All sampling to measure compliance with said standards will be conducted in areas and during time periods appropriate to protect vegetation and livestock.

WAC 18-48-020 DEFINITIONS. (1) Forage - Grasses, pasture and other vegetation that is consumed or is intended to be consumed by livestock.

(2) Cured Forage - Hay, straw, ensilage that is consumed or is intended to be consumed by livestock.

(3) Ambient Air - The surrounding outside air.

(4) Ambient Air Quality Standard - An established concentration, exposure time and frequency of occurrence of a contaminant or multiple contaminants in the ambient air which shall not be exceeded.

WAC 18-48-030 INTENT OF REGULATIONS. Two standards are established by these rules. One shall be for the fluoride content of forage and the other for gaseous fluorides in the ambient air. No person shall cause, let, permit, or allow any emission of elemental or chemically combined fluorine, which either alone or in combination with other fluorides that may be present in forage or the ambient air, to be in excess of the standards in WAC 18-48-040 and -050.

WAC 18-48-040 FORAGE STANDARDS. (1) The fluoride content of forage calculated by dry weight shall not exceed:

(a) Forty parts per million fluoride ion (40 ppm F^-) average for any twelve (12) consecutive months.

(b) Sixty parts per million fluoride ion (60 ppm F^-) each month for more than two (2) consecutive months.

(c) Eighty parts per million fluoride ion (80 ppm F^-) more than once in any two (2) consecutive months.

(2) In areas where cattle are not grazed continually, but are fed cured forage part of the year, the fluoride content of the cured forage shall be used as the forage fluoride content for as many months as it is fed to establish the yearly average.

(3) Cured forage grown for sale as livestock feed shall not exceed forty parts per million fluoride ion (40 ppm F^-) by dry weight after curing or preparing for sale.

WAC 18-48-050 AMBIENT AIR STANDARDS. Gaseous fluorides in the ambient air calculated as HF by volume shall not exceed:

(1) Four and one-half parts per billion (4.5ppb) average for any twelve (12) consecutive hours.

(2) Three and one-half parts per billion (3.5 ppb) average for any twenty-four (24) consecutive hours.

(3) Two parts per billion (2 ppb) average for any seven (7) consecutive days.

(4) One part per billion (1.0 ppb) average for any thirty (30) consecutive days.

WAC 18-48-060 COMPLIANCE WITH STANDARDS. When requested by the Executive Director of the State Board, persons emitting fluorides to the atmosphere shall be required to establish their compliance with WAC 18-48-040 and WAC 18-48-050 by conducting a

monitoring program approved in writing by the Executive Director of the State Board and submitting all data obtained to the Executive Director.

WAC 18-48-070 SAMPLING AND ANALYSIS. (1) Forage samples shall be taken once each calendar month at 25-35 day intervals to determine compliance with WAC 18-48-040.

(2) Gaseous fluoride shall be sampled according to the approved monitoring program, using the sodium bicarbonate tube method.

(3) Samples shall be analyzed by the Technicon Auto Analyzer or the Modified Willard-Winter Distillation Method. The Orion probe may be used to analyze the gaseous ambient air sample when the fluoride is in soluble form. Other sampling and analyses methods which are equivalent in accuracy, sensitivity, reproductibility and applicability under similar conditions may be used after approval by the State Board.

CHAPTER 18-48
APPENDIX 1

METHODS OF COLLECTION AND ANALYSIS FOR FLUORIDES IN FORAGE AND AMBIENT AIR

TABLE OF CONTENTS

SAMPLING AND ANALYSIS FOR FLUORIDE IN AMBIENT AIR AND FORAGE.

DISCUSSION. These methods are adapted, with modification, from procedures which have been used successfully by industry and government laboratories.[1,2,7,10]

Gaseous fluoride is absorbed from an air sample by passing the air across a film of sodium bicarbonate on the inside surface of a glass sampling tube. The coating is removed from the tube by solution in water and the fluoride content determined using a specific ion electrode method.

Particulate matter containing fluorine is collected on a membrane filter. The soluble fluorine compounds are dissolved in water and the fluoride content is determined with a specific ion electrode. The fluorine in the water-insoluble particulate is isolated by steam distilling from sulfuric acid at 165°C and from perchloric acid at 135°C. The fluoride in the distillate is measured by titrating with thorium nitrate to a standard color end point.

Forage samples are dried and ignited to an ash. The fluorine in the ash is isolated by steam distilling from perchloric acid at 135°C and the fluorine content of the distillate is determined spectrophotometrically after reacting with a zirconium-SPADNS reagent.

Automatic analysis of these samples can be made if the results can be shown to compare favorably with those given by the recommended manual methods.[13]

GENERAL PRECAUTIONS. 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 fume. Care must be exercised in the selection, purification and testing of reagents and apparatus, and only minimal exposures of samples should be permitted.

Vessels used for evaporation, ashing, or caustic fusion of samples are first rinsed with warm, dilute acid solution (hydrochloric or nitric), then with distilled water and air dried under clean toweling. Inconel crucibles used for fusion of the ash may require additional cleaning by boiling in 10 per cent (w/v) NaOH for one hour. Glassware is washed with hot detergent solution followed by a rinse in warm, dilute acid. It is finally rinsed with distilled water and dried. All sampling devices, containers, volumetric glassware, reagent solutions, etc. are stored under suitable conditions of protection from airborne dusts and fumes, and are reserved for exclusive use in low-fluoride analysis.

Before proceeding with analysis of samples, blank determinations are repeated until satisfactorily low values (5 ug, 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 analytical procedure with each set of 10 or fewer samples. If samples are handled in larger sets, the ratio of one blank and one standard per 10 samples must be maintained.

FLUORIDE IN AMBIENT AIR AND FORAGE SAMPLING METHODS.

AMBIENT AIR SAMPLING[1]

DISCUSSION. These methods provide a means of separating gaseous

and particulate fluorine compounds.

The reactive gaseous fluorides such as hydrogen fluoride are removed from the air stream with sodium bicarbonate coated on the inside wall of a glass tube. The particulate matter, if collected, is removed by filtration at the tube outlet.

APPARATUS AND REAGENTS. (1) Filter Paper - Whatman No. 32 or equivalent.

(2) Filter Paper Holder - constructed out of aluminum, with all metal parts coated on the inside with Tygon paint mixed 1:10 with thinner. This coating will prevent pickup of fluorine and fluorine compounds by the metal surface. Other holders which are inert to fluorine compounds can be used. An example is the Millipore Swinnex-47 holder made of polypropylene.

(3) Glass Tubing - 4 foot lengths of 7 mm. I.D. tubing with the ends fire polished.

(4) Sample Station - A cabinet at the bottom of the sampling station accommodates the motor, pump and filter holder. A chimney supports and protects the glass tube. A conical rain deflector above the chimney is positioned high enough so that aerosol particulates passing beneath it are still above the glass tube inlet. Design of the sampling shelter may vary to suit individual needs.

(5) Pump - Use an air pump capable of drawing at least one-half cubic foot of air per minute through the tube and filter. (A Gast Model 0440-V2B pump with a by-pass control to regulate the air flow has been found to be satisfactory.)

(6) Dry Gas Meter - Use a meter which is accurate to at least 0.1 cubic foot. (The Sprague Model No. 175 and the Rockwell Model No. 175-S meters have been found to be satisfactory.)

(7) Flowmeter - A calibrated flowmeter can be used to determine air flow rates.

(8) Sodium Bicarbonate ($NaHCO_3$) - 3% solution in distilled water containing a neutral wetting agent. 0.5% polyoxyethylene lauryl alcohol[a] has been found to be satisfactory. Glycerin has also been used.

(9) Soda Lime, 4-8 or 8-16 mesh.

(10) Drying Tower.

PREPARATION OF APPARATUS.

Glass Tubes. Clean all tubes before use with acid cleaning solution or other equivalent cleaner. An alternate method which has been found to be satisfactory is the use of hot detergent, followed by distilled water, methanolic potassium hydroxide (KOH) and finally distilled water.

Discard all tubes that cannot be cleaned.

For the final rinsing, attach all of the tubes in series with rubber tubing. Place an extra tube at the inlet and another at the outlet positions of the tube train, connect the train to distilled water and thoroughly rinse.

Drain the excess water from the tubes. Fill the inlet tube with 3% sodium bicarbonate. Force the solution through the rest of the tube train, thoroughly wetting the inside walls of each tube. Drain and blow out the excess solution.[b]

(a) Brij-35, Atlas Chemical Co., Wilmington, Delaware.

(b) Excess sodium bicarbonate solution is undesirable as it breaks loose from tube wall when dry and is included as particulate material on the filter.

Filter Equipment. Wash and dry all parts of the filter membrane holder. Place the Whatman No. 32 paper or other membrane filter in the holder. Seal the holder by attaching a short length of rubber tubing (about 20 inches) to the inlet and outlet openings.

SAMPLE COLLECTION.

Procedure. At the sampling station, uncap the glass tube and place the tube in the chimney. Connect the tube to the pump inlet and the pump outlet to the meter with short pieces of rubber tubing. Start the pump and adjust the sampling rate to a maximum of 0.5 cubic feet per minute. At the end of the test period, remove the glass tube and replace the caps.

If the particulate matter in the air is to be collected, a filter holder is inserted between the glass absorbtion tube outlet and the pump inlet. All connections are again made with short pieces of rubber tubing and the glass tube is also butted against the metal filter holder inlet. At the end of the test period, remove the glass tube and filter holder and replace all caps.

Data Recording. Include all information relating to the sampling, such as date, starting time, stopping time, sample flow rate, any unusual factors or conditions, temperature at the time of sampling, and barometric pressure at the time of sampling.

FORAGE SAMPLING.(2,12)

Apparatus. (1) One quart glass jars, freezer bags or other inert container that can be used for sample storage. Paper bags may be used if forage leaf surface is dry.

(2) Sharp grass shears or knife.

Sample Collection.

Procedure - Cut the forage with a sharp knife or shears about 2 inches above the ground to avoid contamination by soil particles. Collect about 200 grams of sample; cut it into 1/4" to 1/2" pieces and store it in an appropriate container.

Samples may be stored for up to 5 days before analysis, at refrigeratore temperatures (5°C). Store the samples at 0°C or lower if they are to be kept for longer than 5 days.

Care must be taken to assure that the sample represents the intake of the animal using the forage. In general, the sample should include the main species of forage vegetation in about the same proportion as they grow in the field.

Do not take samples within 100 feet of any road unelss it can be shown that road dust contamination is not a factor.

Data Recording - The following information must be included as part of the sample identification:

(1) Date of sample.
(2) Time of day.
(3) Location of sample.
(4) Types and approximate proportions of vegetation in the sample.
(5) Weather conditions.
(6) Any abnormal factor such as heavy traffic, construction in the area, harvesting nearby, etc.
(7) Original source of sample - is it stacked hay, baled hay, etc.
(8) Name of person who took the sample.

FLUORIDE IN AMBIENT AIR AND FORAGE ANALYSIS METHODS.

WATER SOLUBLE FLUORINE COMPOUNDS - AMBIENT AIR.

DISCUSSION. The ion-selective electrode method[3,4,5] of analysis for fluoride ion has been found to be specific and rapid and is the method of choice for water soluble fluorides.

The water soluble fluorides include those collected from air by the sodium bicarbonate tube method and water soluble portions of the particulate matter collected on the filter.

The fluoride ion selective electrode is a specific ion sensor. The electrode is designed to be used with a standard calomel reference electrode and any modern pH meter having an expanded millivolt scale. The key element in the fluoride ion selective electrode is the doped single lanthanum fluoride crystal across which a potential is established by the presence of fluoride ions. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by $Ag/AgCl,Cl^-(0.3)$, $F^-(0.001M)LaF_3$/test solution//SCE. (SCE - Standard Calomel Electrode.)

The fluoride ion selective electrode can be used to measure the concentration of fluoride in aqueous samples by the use of a calibration curve. The fluoride activity is dependent, however, upon the total ionic strength of the sample, and the electrode does not respond to fluorides which are bound or complexed. These difficulties are largely overcome by the addition of citrate ions to preferentially complex aluminum and the addition of a solution of high total ionic strength to decrease variations in sample ionic strengh.

Polyvalent cations such as Si^{++++}, Al^{+++} will complex fluoride ion. The extent to which complexing takes place depends on the solution pH, the relative levels of the fluoride and the complexing species. The addition of citrate ion will preferentially complex concentrations less than 0.3 ug/liter of aluminum and release the fluoride as the free ion. Also, in acid solution, hydrogen ion forms complexes with fluoride ion, but the complexing is negligible if the pH is adjusted to above pH 5. In alkaline solution the hydroxide ion also interferes with the electrode response to fluoride ion whenever the level of hydroxide ion is greater than one tenth the level of fluoride ion present. However, at pH 8 and below, the hydroxide concentration is 10^{-6} molar or less and no interference occurs with any measurable fluoride concentration.

APPARATUS AND REAGENTS. (1) Expanded scale pH meter of specific meter - No major adjustment of any of the instruments is normally required to use the electrodes in the concentration range 0.2 - 2.0 mg. fluoride per liter. For those instruments with zero at center scale (e.g. some Beckman & Leeds and Northrup meters), it is convenient to set the instrument by adjusting the calibration control so that the 1.0 mg. per liter standard reads at the center zero (100 mv) when the meter is in the expanded scale position. This cannot be done with some meters (e.g. Corning Model 12) which do not have a mv calibration control. If using a specific ion meter, follow the directions of the manufacturer in calibrating the instruments.

(2) Sleeve-type reference electrode - Orion #90-01-100, Beckman #40463, Corning #476012 or equivalent. Fibre-tip reference electrodes are often erratic in very dilute solutions and are not recommended.

(3) Fluoride electrode - Orion or equivalent - A combination fluoride electrode can be used.

(4) Magnetic stirrer - Teflon coated stirring bar.

(5) Stop watch or laboratory timer.

(6) Stock fluoride solution - Dissolve 0.2210 grams of anhydrous sodium fluoride (NaF), in distilled water and dilute to

1000 mls (1.00 ml = 0.100 mg F).

(7) Standard fluoride solution - Dilute 100 ml stock fluoride solution to 1000 ml with distilled water (1.0 ml = 0.01 mg F). Store this reagent in a polyethylene bottle.

(8) Total ionic strength adjustment buffer (TISAB) - Place approximately 500 ml of distilled water in a one-liter beaker. Add 57 ml of glacial acetic acid, 58 grams of sodium chloride, and 0.30 grams of sodium citrate. Stir to dissolve. Place the beaker in a water bath for cooling, insert a calibrated pH electrode and reference electrode into the solution and slowly add approximately 5 M sodium hydroxide (about 150 ml) until the pH is between 5.0 and 5.5 Cool to room temperature. Transfer to a one-liter volumetric flask and dilute with distilled water to one liter. If high aluminum (Al^{+++}) is a problem, the TISAB can be replaced by 0.1 M citric acid adjusted to pH 5.0 to 5.5 with sodium hydroxide.

Sample Preparation

Sodium Bicarbonate Tube - Dissolve the sodium bicarbonate from the tube surfaces with 10 mls of the TISA buffer (refer to the reagent description section) and transfer to a 200 ml volumetric flask. Rinse the tube with water and add the rinsings to the flask. Dilute to 200 mls. Other dilution volumes may also be used.

Particulate Filter - Remove the filter membrane from the holder and place in a 250 ml beaker. Rinse the holder from the inlet side and add the rinsings to the beaker. Add about 50 mls of water and stir for 5 minutes to dissolve any water soluble fluorides on the membrane. Filter through a Whatman No. 32 or equivalent filter paper into a 200 ml volumetric flask. Wash thoroughly and dilute to 200 ml. Other volumetric flasks for other volumes can be used. Save the filter containing the insoluble particulate for fluorine analysis as discussed in the "Analysis Methods" section.

Analytical Procedure - Prepare a series of standards by adding 0.2, 1.0, 5.0, 10.0, 15.0, and 20.0 ml of standard fluoride solution (1 ml = 0.01 mg. F) to a series of 100 ml volumetric flasks. Pipet 50 ml of TISAB solution into each flask and dilute to 0.1, 0.5, 1.0, 1.5, and 2.0 mg. F per liter, respectively. Other standard quantities can be used.

Pipet 50 ml. of sample into a 100 ml. volumetric flask, dilute to 100 mls. with TISAB and mix well. Adjust the temperature of all standards and samples to room temperature, which should preferably be between 23-27°C.

Transfer each standard and sample to a series of 150 ml. plastic beakers. Immerse the electrodes and measure the developed potential while stirring the test solution with a magnetic stirrer. (CAUTION: Stirring of the solution before immersion of the electrodes may entrap air around the crystal and produce erroneous readings or needle fluctuations.) The electrodes must remain in the solution at least three minutes before taking a final millivolt reading. If the sample contains 0.2 mg/liter of fluoride ion, or less, the electrodes must remain in the solution for 10 minutes. The electrodes must be rinsed with distilled water and carefully blotted dry between each reading.

When using an expanded scale pH meter, or specific ion meter, it is necessary to frequently recalibrate the electrode. Recalibration is done by checking the millivolt reading for the 1.0 mg F per liter standard and adjusting the calibration control until the meter reads as before. The calibration should be checked after reading each unknown and after reading each standard when preparing the standard curve.

Plot the millivolt values of the fluoride standards against concentration on 2-cycle semilogarithmic graph paper. Plot mg F

per liter on the logarithmic axis, with the lowest concentration at the bottom of the page. Using the millivolt reading for each unknown sample, determine the corresponding fluoride concentration from this standard curve.

Calculations. Calculate gaseous fluorides as HF by volume at 25°C and 760 mm Hg pressure.

$$\text{HF, ppb by volume (25°C, 760 mm Hg)} = \frac{(A)(B)(D)(G)(2.21\times10^{3})}{(C)(E)(F)}$$

Calculate water soluble particulate fluoride as micrograms F/liter of air at 25!C and 760 mm Hg pressure.

$$\text{F, ug/liter of air (25°C, 760 mm Hg)} = \frac{(A)(B)(D)(G)(2.55)}{(C)(E)(F)}$$

A - mg F/liter, as measured
B - aliquot dilution volume, ml
C - aliquot volume, ml
D - Sample dilution volume, ml
E - Volume of air sampled, liters
F - Barometric pressure at time of sampling, mm Hg
G - Temperature, °K at time of sampling. °K=(°C + 273)

NOTE: The factor 2.21×10^{3} includes F→HF, mg HF→ml HF, standard pressure, standard temperature (25°C) and volume adjustment factors.

The factor 2.55 includes standard pressure, standard temperature (25°C) and weight - volume factors.

ppb - parts per billion.

FLUORIDE IN AMBIENT AIR AND FORAGE ANALYSIS METHODS.

FORAGE AND PARTICULATE MATTER.

Sample Preparation for Distillation

Forage - Mix the sample thoroughly. Determine the moisture content by drying 10-20 grams (accurately weighed) at 80°C for 24 hours or until consecutive weighing shows no further weight loss.

Transfer the balance of the sample to a tared Inconel[(c)] dish and weigh. Sprinkle 1.00 grams of low fluoride calcium oxide[(d)] over the surface of the sample. Add distilled water until the sample is just covered and evaporate to dryness. Infrared lamps can be used to speed the evaporation and as an aid in charring the forage tissues.

Raise the temperature of the hotplate and continue heating until the sample is charred and partially ashed. Most of the ignition of the sample should occur at this stage.

Complete the ashing to a white or gray color at 550°-600°C in an electric furnace which is used only for the ignition of low fluoride materials. Transfer to a dessicator for cooling. Weigh the ash, pulverize, mix and store in a stoppered container.

Transfer approximately one gm of ash to a tared Inconel crucible and weigh accurately. Add about 5 gm of sodium hydroxide pellets, cover the crucible and fuse the contents for a few minutes over a gas burner. This treatment is necessary to assure a quantitative release of fluoride combined with silica in many varieties of vegetation. After cooling the melt, note its color.

(c) Inconel dishes can be obtained from Precision Metal Spinning Co., 9825 Dixie Highway, Clarkston, Mich. Platinum, nickel or other dishes nonreactive to fluoride can be used.

(d) Available on special order from G. Frederick Smith Chemical Co., P.O. Box 23344, Columbus, Ohio 43223.

Blue-green color indicates the presence of manganese and treatment with hydrogen peroxide is required as described in the "Procedure for Single Distillation, Vegation Ash" section. Disintegrate the melt with hot water, washing down the lid and walls of the crucible. Proceed as described in the "Isolation of Fluoride" section.

Particulate Matter - Particulate matter collected during air sampling generally requires fusion with sodium hydroxide for conversion into a soluble form prior to the separation of fluoride by a Willard-Winter distillation. This treatment is also necessary for materials containing fluoride associated with aluminum, for materials high in silica and for many minerals.

Transfer the sample-bearing paper filter or membrane to an Inconel crucible or other resistant metal such as platinum or nickel, moisten with water and make alkaline to phenolphthalein with a known weight of low-fluoride calcium oxide.(d) After evaporation to dryness, ignite the paper in a muffle furnace at a temperature of 550°-600°C until all carbonaceous matter has been oxidized. Control the combustion of filters of the cellulose ester membrane type by drenching with ethanolic sodium hydroxide and igniting with a small gas flame.

Fuse the residue from the ashing of the filter with 2 gm of sodium hydroxide. Dissolve the cold melt in a few ml of water, add a few drops of 30 per cent hydrogen peroxide to oxidize sulfites and boil the solution to destroy excess peroxide. Proceed as described in the "Isolation of Fluoride" section.

ISOLATION OF FLUORIDE (Willard-Winter Distillation)[8,10]

Principle of the Method. The prepared sample is distilled from a strong acid such as sulfuric or perchloric, 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.

Range and Sensitivity. The Willard-Winter distillation method can accommodate quantities of fluoride ranging from 100 mg down to a few micrograms.

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 perchloric acid 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 sulfuric acid at 165°C is used. Large amounts of chloride are separated by precipitation with silver perchlorate following the first distillation. Small amounts are held back in the second distillation from perchloric acid by addition of silver perchlorate solution to the distilling flask.

Precision and Accuracy. 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 per cent of the amount of fluoride present. Under favorable circumstances of sample composition and fluoride range, mean recoveries of approximately 99 per cent with standard deviation of about 2.5 per cent have been reported. Sodium fluoride standards must be distilled to determine the per cent recovery under distillation conditions.

Apparatus and Reagents. (1) Steam Generator - (Figure 1.A) A 2000 ml Florence flask made of heat-resistant glass. The flask is fitted with a stopper; have at least 3 holes for inserting

6 mm OD heat-resistant glass tubing. Through one of the glass tubes, bent at right angles, steam is introduced into the distilling flask. The second tube is a steam release tube (Figure 1,D) which controls the steam pressure. The small piece of rubber tubing which is slipped over the end of the steam release tube is clamped shut during sample distillation. The third tube is a safety tube. If desired, other tubes may be added to permit the steam generator to supply up to 3 distilling flasks. Any suitable heating device may be used.

(2) Distilling Flask - (Figure 1,B) A 250 ml modified Claisen flask made of heat resistant 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 OD heat resistant glass inlet tube for admitting the steam. Any suitable heating device may be used.

(3) Liebig Condenser - (Figure 1,C) Heat resistant glass, 300 mm jacket.

(4) Steam Release Tube - (Figure 1,D).

(5) Thermometer - (Figure 1,E) Partial immersion thermometer having a range of 0° to 200°C.

(6) Support Plate - (Figure 1,F) Metal, ceramic, or hard asbestos board. The plate shall have a perfectly round 5-cm hole in which the distilling flask is placed as shown in Figure 1. The Claisen flask must fit well in the 5-cm 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.

(7) Receiver - (Figure 1,G) 250 or 500 ml volumetric flask, or a 500 ml beaker.

(8) Safety Tube - (Figure 1,H) A 6 mm OD heat-resistant glass tubing, 60 cm long, one end of which is 1 cm from the bottom of the steam generator flask.

(9) Rubber Tubing - (Figure 1,I) For flask connections, made from natural rubber, lengths of rubber tubing shall be kept as short as possible.

(10) Soft Glass Beads - (Figure 1,J) 3 mm diameter, for use in the distilling flask to prevent superheating and to supply silica for the formation of fluosilicic acid during distillation.

(11) Porous Pumice Stones or Boiling Chips - (Figure 1,K).

(12) Pinchcock - (Figure 1,L) to control steam supply from the generator.

(13) Perchloric Acid (70-72 per cent by wt) - Concentrated perchloric acid ($HCLO_4$).[e]

(14) Silver Perchlorate Solution (50 per cent w/v) - Dissolve 100 gm of silver perchlorate ($AgClO_4$) in 100 ml of water.

(15) Sulfuric Acid (96 per cent by wt) - Concentrated sulfuric acid (H_2SO_4).[e]

(16) Water - All references to water shall be understood to mean distilled or deionized water of reagent purity, free of F ion.

Procedure for Forage Ash, Single Distillation. Fill a steam generator about two-thirds full of water. Add a pellet of sodium hydroxide and a few drops of phenolphthalein indicator solution to insure 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.

(e) Acid giving excessively high fluoride blanks requires preboiling at 135°C, with admission of steam, prior to the addition of samples.

Transfer the disintegrated melt to 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 the rubber stopper that contains the thermometer and steam inlet tube in the main neck of the flask. Set the flask in the 5-cm diameter hole in the support plate and connect the outlet to a condenser.

Rinse the sides of the crucible in which the fusion was made with 50 ml of perchloric acid (70 to 72 per cent)[f] and add 1 ml of silver perchlorate solution. 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. If the sample contains manganese, add sufficient (2 to 10 drops) 3 per cent hydrogen peroxide solution to the contents of the distilling flask to reduce manganese dioxide and permanganates. Mix the contents of the flask by gentle shaking and attach the flask to the steam generator. Place a 500 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.

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 400-500 ml of distillate during a period of about 1 1/2 to 2 hours, 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.[g]

Procedure for Particulate Matter, Double Distillation. Fill a steam generator, as directed under "Procedure for Single Distillation." 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 sulfuric acid. 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, 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 the 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 1 1/2 to 2 hours.

(f) Caution. When using perchloric acid, the usual precautions should be taken. Hot concentrated perchloric acid 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 prior to distillation. Precautions for the use of perchloric acid are available in "Chemical Safety Data Sheet SD-11, Perchloric Acid Solution," published by the Manufacturing Chemists' Association of the United States.

(g) Caution. The distilling flasks should be cleaned using only a brush and distilled water. Repeated use of alkaline cleaning solution produces an etched surface that is difficult to clean and tends to retain fluoride.

Add sodium hydroxide solution (10 g/liter) to the distillate until alkaline to phenolphthalein indicator. Evaporate the distillate to 10-15 ml by heating below the boiling point.

The concentrated distillate is redistilled from perchloric acid as directed under "Procedure for Single Distillation." Small quantities of chloride are fixed in the distilling flask by the addition of 1 ml of silver perchlorate solution. A 250 ml quantity of distillate is collected in a volumetric flask.

DETERMINATION OF FLUORIDE, FORAGE DISTILLATE.

Principle of the Method. Reaction of fluoride with the metal ion part of a Zirconium-SPADNS dye complex results in fading of the absorbance of the solution.

Sensitivity and Range. The Zirconium-SPADNS reagent obeys Beer's law over the range of 0.02 ug to 1.40 ug fluoride/ml with a detection limit of about 0.02 ug/ml.

In common with other spectrophotometric methods, this one is temperature sensitive and absorbances must be read within ± 2°C of the temperature at which the calibration curve was established.

Interferences. Moderate variations in acidity of sample solutions will not interfere with the Zirconium-SPADNS reagent.

Many ions interfere with this reagent, but those most likely to be encountered are aluminum, iron, phosphate and sulfate. If these are present above the trace level, their effects must be eliminated.

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.

Precision and Accuracy. 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 sodium fluoride standards indicate that, within the concentration ranges for which the reagents follow Beer's law, a standard deviation of ± 0.015-0.020 ug of fluoride/ml can be expected.

Apparatus and Reagents. (1) Spectrophotometer - An instrument is required which is capable of accepting sample cells of 1 cm to 2.5 cm optical path, and which is adjustable throughout the visible wavelength region. Each spectrophotometer sample cell is given an identification mark and calibrated by reading a portion of the reagent blank solution at the designated wave-length. The determined cell correction is subsequently applied to all absorbance readings made with that cell.

(2) Sodium Fluoride Stock Solution (1 ml=1.0 mg F^-) - Dissolve 2.2105 gm of 100 per cent sodium fluoride (NaF) or the equivalent weight of reagent grade sodium fluoride, in water and dilute to 1 liter. Store in a polyethylene bottle.

(3) Sodium Fluoride Working Standard Solution (1 ml=10 ug F^-) Dilute 5.0 ml of the stock solution to 500 ml. Store in a polyethylene bottle.

(4) SPADNS Stock Solution 4,5-dihydroxy-3 [p-sulfophenyl)azo] 2, 7-napthalene disulfonic acid trisodium salt. Dissolve 0.985 gm SPADNS dye in water and dilute to 500 ml.

(5) SPADNS Reference Solution - Add 10 ml SPADNS stock solution to 100 ml of water. Dilute 7 ml concentrated hydrochloric acid to 10 ml and add to the diluted SPADNS solution. This solution is stable and may be reused indefinitely.

(6) Zirconium Solution - Dissolve 0.133 gm of zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) in 25 ml of water, add 350 ml of concentrated hydrochloric acid, and dilute to 500 ml with water.

(7) Zirconium-SPADNS Reagent - Mix equal volumes of the SPADNS and the zirconium solutions. Cool to room temperature before use. This reagent may be stored in a polyethylene bottle for about six months at room temperature.

Procedure. Dilute a suitable aliquot of the sample solution to 25 ml and add 5.0 ml of Zirconium-SPADNS reagent. Mix and allow to stand for 30 minutes to establish temperature equilibrium before transferring the solution to a spectrophotometer cell (cells of 1 cm to 2.5 cm optical path may be used). Measure the absorbance at 570 mu with the spectrophotometer adjusted to read zero absorbance with the SPADNS Reference Solution.

Prepare a standard series containing from zero to 35 ug of fluoride by pipetting aliquots of the standard sodium fluoride solution (10 ug F^- per ml) into 25 ml volumetric flasks. Add 5 ml of Zirconium-SPADNS reagent to each flask, dilute to 25 mls and mix well. Allow the standards to stand 30 minutes to reach temperature equilibrium. Measure absorbances at 570 millimicrons after adjusting the spectrophotometer to read zero absorbance with the SPADNS Reference Solution. Prepare a calibration curve relating fluoride concentration in micrograms to absorbance values at the selected working temperature.

Calculation. Calculate forage fluoride as parts per million by weight, oven dry basis.

$$\text{ppm F, dry forage} = \frac{(\text{ug F in total distillate})\,(\text{Weight total ash, gms})}{(\text{Weight distilled ash, gms})\,(\text{Weight dry forage, gms})}$$

DETERMINATION OF FLUORIDE, PARTICULATE MATTER DISTILLATE.

Principle of the Method. In the direct titration of fluoride with standard thorium nitrate solution, the sample solution of distillate containing sodium alizarin-sulfonate is buffered at pH 3.0. Upon addition of thorium nitrate, insoluble thorium fluoride is formed. When the endpoint is reached, and all fluoride has reacted, the addition of another increment of thorium nitrate causes the formation of a pink "lake".

In the back titration procedure, the pink "lake" is first formed by addition of sodium alizarin-sulfonate and a slight excess of thorium nitrate 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 sodium fluoride solution until a color match is achieved with the unknown sample.

Range and Sensitivity. The direct titration procedure can accommodate 10 to 0.05 mg fluoride in the total sample. The back titration modifications can measure 50 to about 5 ug fluoride in the total sample. With photometric endpoint detection, direct titration can also be used for the lower ranges.

Interferences. Ions capable of forming insoluble or undissociated compounds with fluorine or with thorium interfere with these titrimetric methods and must be separated. Among the more common of the interfering cations are Al^{+3}, BA^{+2}, Ca^{+2}, Fe^{+3}, Th^{+4}, TiO_2^{+2} VO^{+2}, and Zr^{+4}. The principal interfering anions are PO_4^{-3} and SO_4^{-2}. However, any material which 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 of 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.

Sulfide and sulfite interferences are prevented by preliminary oxidation with 30 per cent hydrogen peroxide in boiling solution, as described in the "Sample Preparation" section. Interference

by free chlorine is eliminated by addition of hydroxylamine hydrochloride solution.

Apparatus and Reagents. (1) Fluorescent Lamp - To provide illumination for titrating.

(2) Microburet - Having 5 ml capacity, 0.01 ml divisions, and a reservoir holding about 50 ml.

(3) Nessler Tubes - Matches 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 40 ml of water, 1 ml of sodium alizarin-sulfonate solution, and 2 ml of 0.05 N hydrochloric acid to the tubes. Add thorium nitrate 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 thorium nitrate 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 shade or intensity.

(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 technique as with the 50 ml tubes, except that the quantities of reagents shall be doubled.

(5) Nessler Tube Rack or Comparator.

(6) Photometric Titrator (optional) - A Beckman Model B Spectrophotometer equipped with an Alcoa Research Laboratories' titration attachment[11] or equivalent. Light from the monochromator passes through a 20.3 cm (8-inch) sample cell to the blue-sensitive phototube mounted at the outboard end of the cell housing. A magnetic stirrer is attached under the cell compartment. The tip of a semi-microburet passes through the cell housing and is immersed in the solution to be titrated. A ball-and-socket joint connects the tip to the buret, facilitating removal of the sample cell. The titration cell is 5.1 cm (2 inches) wide, 7.6 cm (3 inches) deep, and 20.3 cm (8 inches) long.

(7) Buffer-Indicator Solution - Dissolve 0.40 gm of sodium alizarin-sulfonate in about 200 ml of water. Weigh 47.25 gm of monochloracetic acid into a 600 ml beaker and dissolve in 200 ml of water. Combine the two solutions with stirring. Dissolve 10 gm of sodium hydroxide pellets in 50 ml of water, cool to approximately 15° to 20°C, and add to the above solution slowly with stirring. Filter and dilute to 500 ml. Prepare fresh weekly.

(8) Chloroacetate Buffer Solution - Dissolve 9.45 gm of monochloroacetic acid and 2.0 gm of sodium hydroxide (NaOH) in 100 ml of water. This solution is stable for more than two weeks if stored under refrigeration.

(9) Hydrochloric Acid, Standard Solution (0.05 N) - Dilute 4.28 ml of hydrochloric acid (HCl, sp gr 1,19) to 1 liter. The normality of this solution should be exactly equal to that of the 0.05 N sodium hydroxide (NaOH) solution.

(10) Hydroxylamine Hydrochloride Solution - 1 gm of NH_2OH. HCl/100 ml of water.

(11) Phenolphthalein Indicator Solution (0.5 g/liter) - Dissolve 0.5 gm of phenolphthalein in 60 ml of ethyl alcohol and dilute to 1 liter with water.

(12) Sodium Alizarin-sulfonate Solution (0.80 g/liter) - Dissolve 0.40 gm of sodium alizarin-sulfonate in 1000 ml water.[h]

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[h] 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 3-alizarin-sulfonic acid sodium salt. The dye is identified by Color Index No. 58005.

(13) Sodium Alizarin-sulfonate Solution (0.01 g/liter) - Dissolve 0.01 gm of sodium alizarin-sulfonate in 1000 ml of water.

(14) Sodium Fluoride, 100 per cent.

(15) Sodium Fluoride, Standard Solution (1.00 ml=1.00 mg F) - Dissolve 2.2105 gm of sodium fluoride (NaF, 100 per cent) in water, dilute to 1 liter in a volumetric flask and mix. Store in a polyethylene bottle.

(16) Sodium Fluoride, Standard Solution (1 ml=0.01 mg F) - Dilute 10 ml of NaF solution (1.00 ml=1.00 mg F) to 1 liter with water in a volumetric flask, mix, and store in a polyethylene bottle.

Procedure.

Procedure for Direct Titration, High Concentrations (10 to 0.05 mg F in the total sample).

Pipet an aliquot of the distillate into a 400 ml beaker and dilute to 100 ml. Add 1 ml of sodium alizarin-sulfonate solution (0.80 g/liter), and then sodium hydroxide solution (10 g/liter) dropwise until a pink color is obtained. Discharge the pink color by adding 0.05 N hydrochloric acid dropwise. Add 1 ml of chloroacetate buffer solution dropwise, and titrate with thorium nitrate solution (1 ml=1.9 mg F) to a faint, persistent pink endpoint. Determine a blank obtained by carrying the same amount of all reagents through the entire procedure, including ashing and distillation.

Procedure for Back Titration, Medium Concentration (0.05 to 0.01 mg F in the total sample).

Transfer 50 ml of the distillate into a 50 ml Nessler tube, add 1 ml of sodium alizarin-sulfonate solution (0.01 g/liter) and sufficient 0.05 N sodium hydroxide solution to produce a pink color. Note precisely the volume of 0.05 N sodium hydroxide solution required for neutralization. Then discard the titrated solution. If more than 4 ml of 0.05 N sodium hydroxide solution is required, make the remaining distillate alkaline, evaporate to 10 to 15 ml, and transfer it to a distilling flask. Repeat the distillation, precautions being taken to reduce the amount of perchloric acid distilled over.

Transfer another 50-ml portion of distillate into a 50 ml Nessler tube (sample tube) and add 1 ml of sodium alizarin-sulfonate solution (0.01 g/liter). Adjust the acidity with 0.05 N hydrochloric acid until the equivalent of exactly 2 ml of acid is present; that is, 2 ml minus the number of ml of 0.05 N sodium hydroxide solution required for neutralization as described. If between 2 ml and 4 ml of 0.05 N sodium hydroxide solution were required for neutralization, omit the addition of hydrochloric acid to the distillate. Add thorium nitrate solution (0.25 g/liter) from a microburet until a faint pink color appears. Note the volume of thorium nitrate solution required, and save the Nessler tube for comparison with the standard.

Pour 50 ml of water into a 50-ml Nessler tube (standard tube) and add 1 ml of sodium alizarin-sulfonate solution (0.01 g/liter). If neutralization of the sample required 2 ml or less of 0.05 N sodium hydroxide solution, pipet exactly 2 ml of 0.05 N hydrochloric acid into the standard tube. If the 50 ml aliquot of the distillate required more than 2 ml of 0.05 N sodium hydroxide solution 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.

From a microburet add sodium fluoride solution (1 ml = 0.01 mg F) equivalent to about 80 per cent of the fluoride

present in the sample aliquot, as indicated by the thorium nitrate solution required. Mix thoroughly, add the same volume of thorium nitrate solution as that required for titration of the sample aliquot, and again mix thoroughly. The color in the standard tube will be deeper than that in the sample tube.

From the microburet, continue to add sodium fluoride solution (1 ml=0.01 mg F) 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 1 or 2 drops of sodium fluoride solution (1 ml=0.01 mg F) to the standard tube. If the colors were originally matched, the color in the standard tube will be distinctly lighter in shade than in the sample tube.

Determine a blank by carrying the same amount of all reagents through the entire procedure including ashing and distillation. With proper attention to details, blanks of 5 ug of fluoride, or less, can be obtained.

Procedure for Back Titration, Low Concentrations (less than 0.01 mg F in the 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 perchloric acid 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:

Add 2 ml of sodium alizarin-sulfonate solution (0.01 g/liter) and neutralize the acid by adding 0.05 N sodium hydroxide solution until a pink color is produced. Add 4 ml of 0.05 N hydrochloric acid and sufficient thorium nitrate solution (0.25 g/liter) to provide a faint pink color. Compare the treated distillate portion with a standard of equal total volume containing 2 ml of sodium alizarin-sulfonate solution (0.01 g/liter), 4 ml of hydrochloric acid and the same volume of thorium nitrate solution (0.25 g/liter) as is required to produce the pink color in the sample tube. Add sodium fluoride 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.

Procedure for Photometric Titration. Transfer the distillate to a 20.3 cm (8-inch) titration cell and add 5 ml of hydroxylamine hydrochloride solution. Adjust, if necessary, to pH 3.6 with 0.05 N perchloric acid, and then add 5 ml of buffer-indicator solution.(i)

(i) 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 acidity of the distillate is less than pH 3.5, 0.05 N, sodium hydroxide may be used 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 sodium hydroxide for neutralization produces a slight change in the factor due to the sodium perchlorate formed.

Place the cell in the titrating attachment, immerse the buret tip, and start the stirring motor. Close the titrator lid, set the wave length to 525 mu, and the sensitivity knob to the proper position (usually 1). Close the shutter and adjust the slit width to give a transmittance reading of 100.

Titrate with standard thorium nitrate (0.01 N solution) to a transmittance reading of 75 per cent. Record the volume to the nearest 0.005 ml.

Deduct a blank obtained by carrying the same amount of all reagents through the entire procedure, including ashing and distillation. Determine the amount of fluoride present from a calibration curve.

Standardization of Thorium Nitrate Solutions.

Thorium Nitrate, Standard Stock Solution (1 ml=1.9 mg F).

Weigh 0.100 gm of sodium fluoride 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 strength of the thorium nitrate solution in terms of mg of fluoride ion/ml of solution as follows:

$$\text{Fluoride ion, mg/ml} = \frac{(20 \text{ mg NaF})\ (C)}{A - B}$$

Where: A = ml of $Th(NO_3)_4 \cdot 4H_2O$ solution required for titration of the fluoride.
B = ml of $Th(NO_3)_4 \cdot 4H_2O$ solution required for titration of the blank.
C = factor for NaF to F = 0.4524

Thorium Nitrate Solution, 0.01 N (1 ml=0.19 mg F) - Photometric Titration Solution). Pipet aliquots of standard sodium fluoride solution covering the range 10 to 1000 ug of fluoride into 500 ml volumetric flasks and dilute to volume. Transfer to a 20.3 cm titration cell, add 5 ml of hydroxylamine hydrochloride solution, and adjust to pH 3.6 with 0.05 N perchloric acid. Add 5 ml of buffer-indicator solution and titrate as described in the "Procedure for Photometric Titration" section.

Calculation. Calculate particulate fluoride[j] as milligrams per cubic meter at 25°C and 760 mm Hg pressure:

$$\text{Particulate fluoride}^{(j)} \text{ milligrams F/m}^3 = \frac{(A-B)(C)\ (D)\ (E)\ (F)}{(G)\ \ (P)\ \ (V)}$$

A - ml titrating solution[k] used to titrate sample aliquot.
B - ml titrating solution used to titrate reagent blank.
C - fluoride equivalent of titrating solution as mg F/ml solution.
D - ml total distillate collected.[l]

(j) Designate whether this is total particulate or water insoluble particulate.

(k) The term "titrating solution" refers to either the $Th(NO_3)_4$ solution used in accordance with the "Procedure for Direct Titration", or the NaF solution (1 ml=0.01 mg F) used in "Procedure for Back Titration".

(l) The volume or 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 "Procedure for Back Titration, Low Concentrations". If this procedure applies, for each portion of distillate titrated, the value of G is equal to the value of D.

E - (1000 liters/meter^3) (760 mm Hg)÷(273+25)°= 2550.
F - 273 + sampling temperature in °C.
G - ml distillate titrated.[k]
P - barometer pressure at time of sampling, mm Hg.
V - volume of atmosphere sampled.

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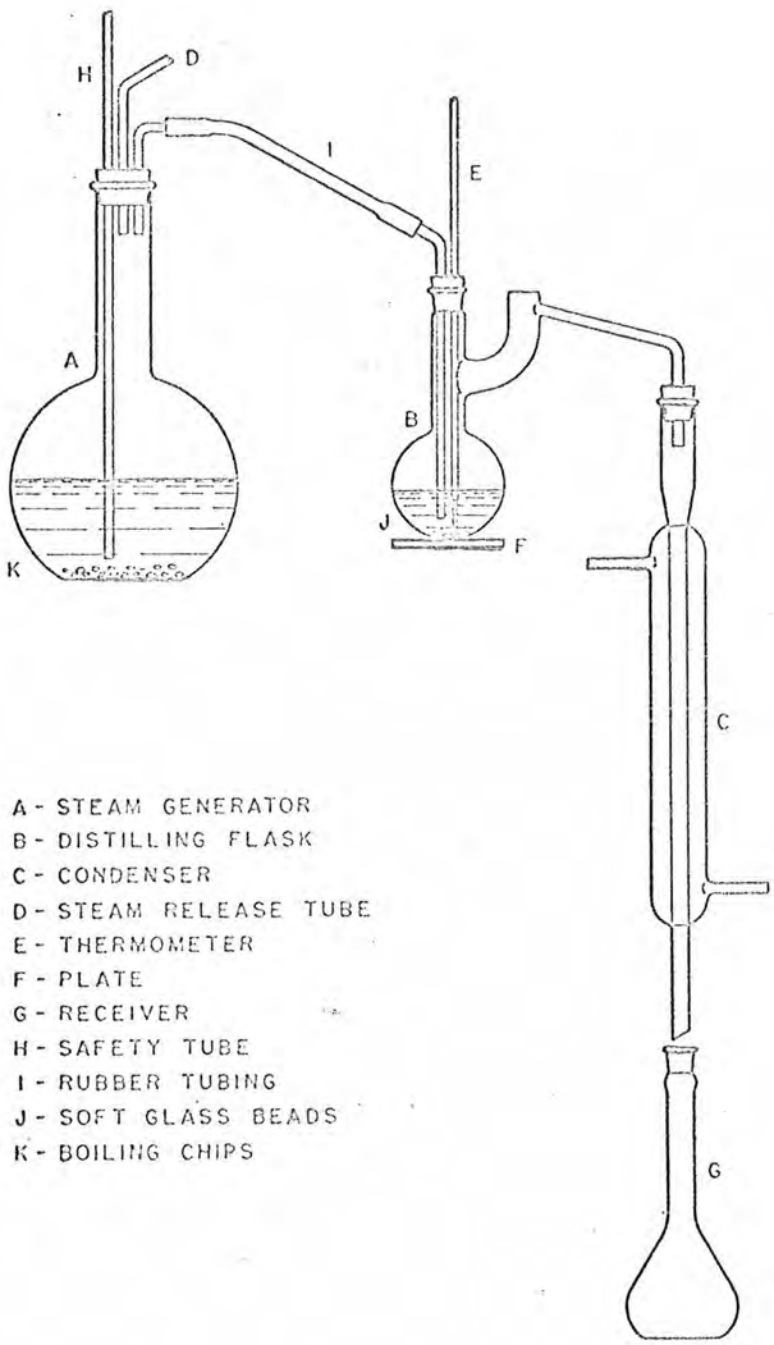
Figure 1 - Apparatus for distillation of fluoride.



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 - SOFT GLASS BEADS
K - BOILING CHIPS