Table 4500-CN^-:11. Results of the ISO 17690 Collaborative Testing

Sample	Matrix[a]	l	n	o (%)	X (µg/L)	$\bar{\bar{x}}$ (µg/L)	η (%)	s_R (µg/L)	$C_{V,R}$ (%)	s_r (µg/L)	$C_{V,R}$ (%)
1	Groundwater	11	22	8.33	822	815	99.1	60.9	7.47	8.30	1.02
2	Surface water	11	22	8.33	409	398	97.3	32.5	8.16	6.16	1.55
3	Potable water	11	22	8.33	195	202	104	16.0	7.92	1.76	0.87
4	Leach solution	11	22	8.33	167	179	93.3	12.8	7.15	2.28	1.27
5	Effluent	11	22	8.33	9.4	8.00	85.0	2.95	36.9	0.51	6.38

l = Number of laboratories after outlier rejection
n = Number of individual test results after outlier rejection
o = Percentage of outliers
X = Assigned value
$\bar{\bar{x}}$ = Overall mean of results (without outliers)
η = Recovery rate
S_R = Reproducibility standard deviation
$C_{V,R}$ = Coefficient of variation of reproducibility
S_r = Repeatability standard deviation
$C_{V,r}$ = Coefficient of variation repeatability
[a] Origin of the samples:
Sample 1 spiked, Metallurgical tailings solution, Nevada.
Sample 2 spiked, Cherry Creek, Centennial, Colorado.
Sample 3 spiked, Denver aquifer, Parker, Colorado.
Sample 4 spiked, Heap leach drain down solution, Nevada.
Sample 5 unspiked, laboratory treated metallurgical tailings filtrate.

With permission, ISO 17690:2015. Water quality: Determination of available free cyanide (pH 6) using flow injection analysis (FIA), gas-diffusion and amperometric detection. Geneva (Switzerland): International Organization for Standardization; 2015.

Some instrument systems allow first order quadratic fits for the working curve range, as long as at least 6 standards and a blank are used for the curve fit over the method's working range.

6. Precision and Bias

Collaborative precision studies: An ASTM collaborative study was carried out in 8 laboratories on 3 Youden Pair samples. An ISO collaborative study was carried out in 12 laboratories on 5 matrix samples. Results are summarized in Table 4500-CN^-:10 and Table 4500-CN^-:11.

References

1. ASTM D7237-18. Standard test method for free cyanide with aquatic free cyanide with flow injection analysis (FIA) utilizing gas diffusion separation and amperometric detection. West Conshohocken (PA): ASTM International; 2018.
2. ISO 20950-1:2018. Interlaboratory Trial Results for ISO/CD 20950. Water quality. Determination of available weak and dissociable (WAD) cyanide. Part 1: Method using ligand exchange, flow injection analysis (FIA), gas-diffusion and amperometric detection. Geneva, Switzerland: International Organization for Standardization (ISO). 2018.

4500-F⁻

FLUORIDE

Approved by Standard Methods Committee, 1997. Editorial revisions, 2021. Joint Task Group: Scott Stieg (chair), Bradford R. Fisher, Owen B. Mathre, Theresa M. Wright.

4500-F⁻ A. INTRODUCTION

Fluoride may occur naturally in water or it may be added in controlled amounts. Some fluorosis may occur when the fluoride level exceeds the recommended limits. In rare instances, the naturally occurring fluoride concentration may approach 10 mg/L.

Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation procedure.

1. Preliminary Treatment

Among the methods suggested for determining fluoride ion (F$^-$) in water, the electrode and colorimetric methods are the most satisfactory. Because both methods are subject to errors due to interfering ions (Table 4500:F$^-$:1), it may be necessary to distill the sample as directed in 4500-F$^-$ B before making the determination. When interfering ions are not present in excess of the tolerance of the method, the fluoride determination may be made directly without distillation.

2. Selection of Method

The electrode methods (4500-F$^-$ C and G) are suitable for fluoride concentrations from 0.1 to more than 10 mg/L. The buffer solution frees the electrode method from most interferences that adversely affect the SPADNS colorimetric method and necessitate preliminary distillation. Some substances in industrial wastes, such as fluoborates, may be sufficiently concentrated to present problems in electrode measurements and are not measured without a preliminary distillation. Fluoride measurements can be made with an ion-selective electrode and either an expanded-scale pH meter or a specific ion meter, usually without distillation, in the time necessary for electrode equilibration.

The SPADNs method (4500-F$^-$ D) has a linear analytical range of 0 to 1.40 mg/L F$^-$. The use of a nonlinear calibration can extend the range to 3.5 mg/L F$^-$. Color development is virtually instantaneous. Color determinations are made photometrically, using either a filter photometer or a spectrophotometer. A curve developed from standards is used for determining the fluoride concentration of a sample.

Fluoride also may be determined by the automated complex-one method, 4500-F$^-$ E.

Ion chromatography (Section 4110) is an acceptable method if weaker eluents are used to separate fluoride from interfering peaks or fluoride can be determined by capillary ion electrophoresis (Section 4140).

The flow injection method (4500-F$^-$ G) is a convenient automated technique for analyzing large numbers of samples.

3. Sampling and Storage

Preferably use polyethylene bottles for collecting and storing samples for fluoride analysis. Glass bottles are satisfactory if previously they have not contained high-fluoride solutions. Always rinse the bottle with a portion of sample.

For the SPADNs method, never use an excess of dechlorinating agent. Dechlorinate with sodium arsenite rather than sodium thiosulfate when using the SPADNS method because the latter may produce turbidity that causes erroneous readings.

4500-F$^-$ B. PRELIMINARY DISTILLATION STEP

1. Discussion

Fluoride can be separated from other nonvolatile constituents in water by conversion to hydrofluoric or fluosilicic acid and subsequent distillation. The conversion is accomplished by using a strong, high-boiling acid. To protect against glassware etching, hydrofluoric acid is converted to fluosilicic acid by using soft glass beads. Quantitative fluoride recovery is approached by using a relatively large sample. Acid and sulfate carryover are minimized by distilling over a controlled temperature range.

Distillation separates fluoride from most water samples. Some tightly bound fluoride, such as that in biological materials, may require digestion before distillation, but water samples seldom require such drastic treatment. Distillation produces a distillate volume equal to that of the original water sample, so usually it is not necessary to incorporate a dilution factor when expressing analytical results. The distillate will be essentially free of substances that might interfere with the fluoride determination if the apparatus used is adequate and distillation has been carried out properly. The only common volatile constituent likely to cause interference with colorimetric analysis of the distillate is chloride. When the concentration of chloride is high enough to interfere, add silver sulfate to the sulfuric acid distilling mixture to minimize the volatilization of hydrogen chloride.

Caution: Heating an acid–water mixture can be hazardous if precautions are not taken. Mix acid and water thoroughly before heating. The use of a quartz heating mantle and a magnetic stirrer in the distillation apparatus simplifies the mixing step.

2. Apparatus

a. Distillation apparatus consisting of a 1-L round-bottom long-neck borosilicate glass boiling flask, a connecting tube, an efficient condenser, a thermometer adapter, and a thermometer that can be read to 200 °C. Use standard taper joints for all connections in the direct vapor path. Position the thermometer so the bulb always is immersed in boiling mixture. Purchase apparatus that can be quickly disassembled for easy sample addition. Substituting a thermoregulator and necessary circuitry for the thermometer is acceptable and provides some automation.

Alternative types of distillation apparatus may be used. Carefully evaluate any apparatus for fluoride recovery and sulfate carryover. The critical points are obstructions in the vapor path and trapping of liquid in the adapter and condenser. (The condenser should have a vapor path with minimum obstruction. A double-jacketed condenser, with cooling water in the outer jacket and the inner spiral tube, is ideal, but other condensers are acceptable if they have minimum obstructions. Avoid using Graham-type condensers.) Avoid using an open flame as a heat source if possible, because heat applied to the boiling flask above the liquid level causes superheating of vapor and subsequent sulfate carryover.

Caution: Regardless of apparatus used, provide for thorough mixing of sample and acid. Heating a nonhomogenous acid–water mixture results in bumping or possibly a violent explosion.

The preferred apparatus is illustrated in Figure 4500-F$^-$:1.

b. Quartz hemispherical heating mantle, for full-voltage operation.

c. Magnetic stirrer, with PTFE-coated stirring bar.

d. Soft glass beads.

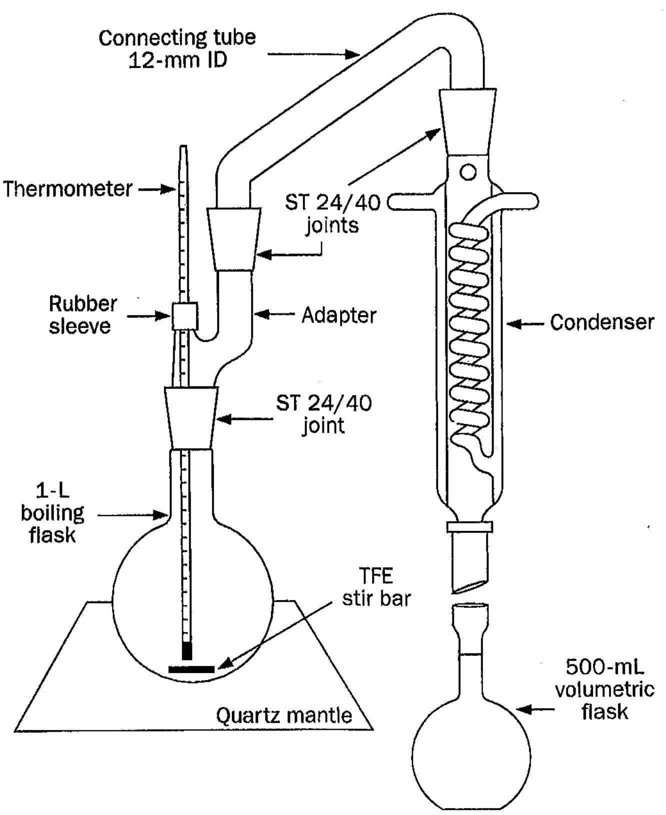

Figure 4500-F$^-$:1. Direct distillation apparatus for fluoride.

3. Reagents

a. Sulfuric acid (H_2SO_4), conc, reagent grade.

b. Silver sulfate (Ag_2SO_4), crystals, reagent grade.

4. Procedure

a. Place 400 mL reagent water in the distillation flask and, with the magnetic stirrer operating, carefully add 200 mL conc H_2SO_4. Keep stirrer in operation throughout distillation. Add a few glass beads and connect the apparatus as shown in Figure 4500-F$^-$:1, making sure all joints are tight. Begin heating and continue until flask contents reach 180 °C (because of heat retention by the mantle, it is necessary to discontinue heating when the temperature reaches 178 °C to prevent overheating). Discard the distillate. This process removes fluoride contamination and adjusts the acid–water ratio for subsequent distillations.

b. After the acid mixture remaining in the steps outlined in paragraph *a* above, or previous distillations, has cooled to 80 °C or below, add 300 mL sample with stirrer operating, and distill until the temperature reaches 180 °C. To prevent sulfate carryover, turn off the heat before 178 °C. Retain the distillate for analysis.

c. Add 5 mg of Ag_2SO_4 per milligram of Cl to the distillation flask when the Cl concentration is high enough to interfere (Table 4500-F$^-$:1).

d. Use H_2SO_4 solution in the flask repeatedly until contaminants from samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check acid suitability periodically by distilling standard fluoride samples and analyzing for both fluoride and sulfate. After distilling the samples containing more than 3 mg/L F$^-$, flush the still by adding 300 mL reagent water, redistill, and combine the 2 fluoride distillates. If necessary, repeat flushing until the fluoride content of the last distillate is at a minimum. Include additional fluoride recovered with that of the first distillation. After periods of inactivity, similarly flush the still and discard the distillate.

5. Interpretation of Results

The recovery of fluoride is quantitative within the accuracy of the methods used for its measurement.

Bibliography

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4500-F$^-$ C. Ion-Selective Electrode Method

1. General Discussion

a. Principle: The fluoride electrode is an ion-selective sensor. The key element in the fluoride electrode is the laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by:

$$Ag \mid AgCl^- (0.3\ M),\ F^- (0.001\ M) \mid LaF_3 \mid \text{test solution} \mid \text{reference electrode}$$

The fluoride electrode can be used with a standard calomel reference electrode and almost any modern pH meter having an expanded millivolt scale. Calomel electrodes contain both metallic and dissolved mercury; therefore, dispose of them only in approved sites or recycle. For this reason, the Ag/AgCl reference electrode is preferred.

The fluoride electrode measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution's total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjusts pH, and breaks up complexes. In effect, the electrode measures concentration.

b. Interference: Table 4500-F$^-$:1 lists common interferences. Fluoride forms complexes with several polyvalent cations, notably aluminum and iron. The extent to which complexation takes place depends on solution pH, relative levels of fluoride, and complexing species. However, 1,2-cyclohexylenediaminetetraacetic acid (CDTA), a component of the buffer, preferentially complexes interfering cations and release free fluoride ions. Concentrations

Table 4500-F$^-$:1. Concentration of Some Substances Causing 0.1-mg/L Error at 1.0 mg/L F$^-$ in Fluoride Methods

	4500-F$^-$ C (Electrode)		4500-F$^-$ D (SPADNS)	
Substance	Concentration (mg/L)	Type of Error[a]	Concentration (mg/L)	Type of Error
Alkalinity ($CaCO_3$)	7 000	+	5 000	–
Aluminum (Al^{3+})	3.0	–	0.1[a]	–
Chloride (Cl^-)	20 000	ND	7 000	+
Chlorine	5 000	ND	ND	Remove completely with arsenite
Color & turbidity		ND	ND	Remove or compensate for
Iron	200	–	10	–
Hexametaphosphate ($[NaPO_3]_6$)	50 000	ND	1.0	+
Phosphate (PO_4^{3-})	50 000	ND	16	+
Sulfate (SO_4^{2-})	50 000	–	200	–

+ = positive error; – = negative error; ND = not detected or no measurable error.

[a] On immediate reading. Tolerance increases with time: after 2 h, 3.0; after 4 h, 30.

of aluminum, the most common interference, up to 3.0 mg/L can be complexed preferentially. In acid solution, F forms a poorly ionized HF · HF complex but the buffer maintains a pH above 5 to minimize hydrogen fluoride complex formation. In alkaline solution, hydroxide ion also can interfere with electrode response to fluoride ion whenever the hydroxide ion concentration is greater than one-tenth the concentration of fluoride ion. At the pH maintained by the buffer, no hydroxide interference occurs.

Fluoborates are widely used in industrial processes. Dilute solutions of fluoborate or fluoboric acid hydrolyze to liberate fluoride ion, but in concentrated solutions (e.g., electroplating wastes) hydrolysis does not occur completely. Distill such samples or measure fluoborate with a fluoborate-selective electrode. Also distill the sample if the dissolved solids concentration exceeds 10 000 mg/L.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Expanded-scale or digital pH meter or ion-selective meter.

b. Sleeve-type reference electrode: Do not use fiber-tip reference electrodes because they exhibit erratic behavior in very dilute solutions.

c. Fluoride electrode.

d. Magnetic stirrer, with TFE-coated stirring bar.

e. Timer.

3. Reagents

a. Stock fluoride solution: Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in reagent water and dilute to 1000 mL; 1.00 mL = 100 mg F$^-$.

b. Standard fluoride solution: Dilute 100 mL stock fluoride solution to 1000 mL with reagent water; 1.00 mL = 10.0 µg F$^-$.

c. Fluoride buffer: Place approximately 500 mL reagent water in a 1-L beaker and add 57 mL glacial acetic acid, 58 g NaCl, and 4.0 g 1,2 cyclohexylenediaminetetraacetic acid (CDTA) also known as 1,2 cyclohexylenedinitrilotetraacetic acid. Stir to dissolve. Place the beaker in a cool water bath and add slowly 6 N NaOH (about 125 mL) while stirring, until the pH is between 5.0 and 5.5. Transfer to a 1-L volumetric flask and add reagent water to the mark. This buffer, as well as a more concentrated version, is available commercially. In using the concentrated buffer, follow the manufacturer's directions.

4. Procedure

a. Instrument calibration: No major adjustment of any instrument normally is required to use electrodes in the range of 0.2 to 2.0 mg/L F$^-$. For those instruments with zero at center scale, adjust calibration control so the 1.0 mg/L F$^-$ standard reads at the center zero (100 mV) when the meter is in the expanded-scale position. This cannot be done on some meters that do not have a millivolt calibration control. To use a selective-ion meter, follow the manufacturer's instructions.

b. Preparation of fluoride standards: Prepare a series of standards by diluting with reagent water 5.0, 10.0, and 20.0 mL of standard fluoride solution to 100 mL with reagent water. These standards are equivalent to 0.5, 1.0, and 2.0 mg/L F$^-$.

c. Treatment of standards and sample: In 100-mL beakers or other convenient containers, add by volumetric pipet from 10 to 25 mL standard or sample. Bring standards and sample to same temperature, preferably room temperature. Add an equal volume of buffer. The total volume should be sufficient to immerse the electrodes and permit operation of the stirring bar.

d. Measurement with electrode: Immerse electrodes in each of the fluoride standard solutions and measure the developed potential while stirring on a magnetic stirrer. Check for air bubbles after immersing the electrodes because entrapped air around the crystal can produce erroneous readings or needle fluctuations. Let electrodes remain in the solution 3 min (or until reading is constant) before taking a final millivolt reading. A layer of insulating material between stirrer and beaker minimizes solution heating. Withdraw electrodes, rinse with reagent water, and *blot dry* between readings. (**Caution: Blotting may poison electrode if not done gently.**) Repeat measurements with samples.

When using an expanded-scale pH meter or selective-ion meter, frequently recalibrate the electrode by checking potential reading of the 1.00-mg/L F$^-$ standard and adjusting the calibration control, if necessary, until the meter reads as before.

If a direct-reading instrument is not used, plot the potential measurement of fluoride standards against concentration on 2-cycle semilogarithmic graph paper. Plot milligrams F^- per liter on the logarithmic axis (ordinate), with the lowest concentration at the bottom of the graph. Plot millivolts on the abscissa. From the potential measurement for each sample, read the corresponding fluoride concentration from the standard curve.

The known-additions method may be substituted for the calibration method described. Follow the directions of the instrument manufacturer.

Selective-ion meters may necessitate using a slightly altered procedure, such as preparing 1.00 and 10.0 mg/L F^- standards or some other concentration. Follow the manufacturer's directions. Commercial standards, often already diluted with buffer, frequently are supplied with the meter. Verify the stated fluoride concentration of these standards by comparing them with standards prepared by the analyst.

5. Calculation

$$\text{mg/L } F^- = \frac{\mu\text{g } F^-}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 0.850 mg/L F^- in distilled water was analyzed in 111 laboratories by the electrode method, with a relative standard deviation of 3.6% and a relative error of 0.7%.

A second synthetic sample containing 0.750 mg/L F^-, 2.5 mg/L $(NaPO_3)_6$, and 300 mg alkalinity per liter added as $NaHCO_3$, was analyzed in 111 laboratories by the electrode method, with a relative standard deviation of 4.8% and a relative error of 0.2%.

A third synthetic sample containing 0.900 mg/L F^-, 0.500 mg/L Al, and 200 mg/L SO_4^{2-} was analyzed in 13 laboratories by the electrode method, with a relative standard deviation of 2.9% and a relative error of 4.9%.

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4500-F⁻ D. SPADNS METHOD

1. General Discussion

a. Principle: The SPADNS colorimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}) and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.

The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

b. Interference: Table 4500-F⁻:1 lists common interferences. Because these are neither linear in effect nor algebraically additive, mathematical compensation is impossible. Whenever any single substance is present in sufficient quantity to produce an error of 0.1 mg/L or whenever the total interfering effect is in doubt, distill the sample. Also distill colored or turbid samples. In some instances, sample dilution or adding appropriate amounts of interfering substances to the standards may be used to compensate for the interference effect. If alkalinity is the only significant interference, neutralize it with either hydrochloric or nitric acid. Residual chlorine interferes and must be removed before analysis.

Volumetric measurement of sample and reagent is extremely important to analytical accuracy. Use samples and standards at the same temperature or at least within 2 °C. Maintain constant temperature throughout the color development period. Prepare different calibration curves for different temperature ranges.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 570 nm, providing a light path of at least 1 cm.

b. Filter photometer, providing a light path of at least 1 cm and equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm.

3. Reagents

a. Standard fluoride solution: Prepare as directed in the electrode method, 4500-F⁻ C.3*b*.

b. SPADNS solution: Dissolve 958 mg SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt, in reagent water and dilute to 500 mL. This solution is stable for at least 1 year if protected from direct sunlight.

c. Zirconyl-acid reagent: Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in about 25 mL reagent water. Add 350 mL conc HCl and dilute to 500 mL with reagent water.

d. Acid zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 years.

e. Reference solution: Add 10 mL SPADNS solution to 100 mL reagent water. Dilute 7 mL conc HCl to 10 mL and add to the diluted SPADNS solution. The resulting solution, used for setting the instrument reference point (zero), is stable for at least 1 year. Alternatively, use a prepared standard of 0 mg/L F^- as a reference.

f. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ and dilute to 1 L with reagent water. **(Caution: Toxic—avoid ingestion.)**

4. Procedure

a. Preparation of standard curve: Prepare fluoride standards in the range of 0 to 1.40 mg/L F^- by diluting appropriate quantities of standard fluoride solution to 50 mL with reagent water. Pipet 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL mixed acid-zirconyl-SPADNS reagent, to each standard and mix well. Avoid contamination. Set the photometer to zero absorbance with the reference solution and obtain absorbance readings of the standards. Plot a curve of the milligrams fluoride–absorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. As an alternative to using a reference, set the photometer at some convenient point (0.300 or 0.500 absorbance) with the prepared 0 mg/L F^- standard.

b. Sample pretreatment: If the sample contains residual chlorine, remove it by adding 1 drop (0.05 mL) $NaAsO_2$ solution per 0.1 mg residual chlorine and mix. (Sodium arsenite concentrations of 1300 mg/L produce an error of 0.1 mg/L at 1.0 mg/L F^-.)

c. Color development: Use a 50.0-mL sample or a portion diluted to 50 mL with reagent water. Adjust the sample temperature to that used for the standard curve. Add 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL acid-zirconyl-SPADNS reagent. Mix well and read the absorbance, first setting the reference point of the photometer as above. If the absorbance falls beyond the range of the standard curve, repeat using a diluted sample.

5. Calculation

$$\text{mg/L F}^- = \frac{A}{\text{mL sample}} \times \frac{B}{C}$$

where:

A = µg F^- determined from plotted curve,
B = final volume of diluted sample (mL), and
C = volume of diluted sample used for color development (mL).

When the prepared 0 mg/L F^- standard is used to set the photometer, alternatively calculate fluoride concentration as follows:

$$\text{mg/L F}^- = \frac{A_0 - A_x}{A_0 - A_1}$$

where:

A_0 = absorbance of the prepared 0 mg/L F^- standard,
A_x = absorbance of the prepared sample, and
A_1 = absorbance of a prepared 1.0 mg/L F^- standard.

6. Precision and Bias

A synthetic sample containing 0.830 mg/L F^- and no interference in distilled water was analyzed in 53 laboratories by the SPADNS method, with a relative standard deviation of 8.0% and a relative error of 1.2%. After direct distillation of the sample, the relative standard deviation was 11.0% and the relative error 2.4%.

A synthetic sample containing 0.570 mg/L F^-, 10 mg/L Al, 200 mg/L SO_4^{2-}, and 300 mg total alkalinity per liter was analyzed in 53 laboratories by the SPADNS method without distillation, with a relative standard deviation of 16.2% and a relative error of 7.0%. After direct distillation of the sample, the relative standard deviation was 17.2% and the relative error 5.3%.

A synthetic sample containing 0.680 mg/L F^-, 2 mg/L Al, 2.5 mg/L $(NaPO_3)_6$, 200 mg/L SO_4^{2-}, and 300 mg total alkalinity per liter was analyzed in 53 laboratories by direct distillation and SPADNS methods with a relative standard deviation of 2.8% and a relative error of 5.9%.

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4500-F^- E. COMPLEXONE METHOD

1. General Discussion

a. Principle: The sample is distilled in the automated system, and the distillate is reacted with alizarin fluorine blue-lanthanum reagent to form a blue complex that is measured colorimetrically at 620 nm.

b. Interferences: Interferences normally associated with the determination of fluoride are removed by distillation.

c. Application: This method is applicable to potable, surface, and saline waters as well as domestic and industrial wastewaters. The range of the method, which can be modified by using the adjustable colorimeter, is 0.1 to 2.0 mg/L F^-.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

An example of the required continuous-flow analytical instrument consists of the interchangeable components in the number and manner indicated in Figure 4500-F^-:2.

3. Reagents

a. Standard fluoride solution: Prepare in appropriate concentrations from 0.10 to 2.0 mg/L F^- using the stock fluoride solution (see 4500-F^- C.3*a*).

b. Distillation reagent: Add 50 mL conc H_2SO_4 to about 600 mL reagent water. Add 10.00 mL stock fluoride solution (see 4500-F^- C.3*a*; 1.00 mL = 100 µg F^-) and dilute to 1000 mL.