Hach Company SPADNS 2 (Arsenic-Free) Fluoride Method 10225 – Spectrophotometric Measurement of Fluoride in Water and Wastewater

Hach Company SPADNS 2 Fluoride Method 10225

Revision 1.0
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Spectrophotometric Measurement of Fluoride in Water and Wastewater

1.0 Scope and Application

1.1 These procedures cover the determination of fluoride in drinking water, surface and saline waters, domestic and industrial wastes.

1.2 The method is applicable in the range from 0.10 to 2.00 mg F- /L.

1.3 This method is equivalent to SM 4500-F^- D and EPA 340.1 for the purposes of regulatory reporting of fluoride.

2.0 Summary of Method

2.1 Fluoride reacts with a zirconium SPADNS dye. The loss of color during this reaction is proportional to the fluoride concentration in the sample. The SPADNS 2 reagent contains a non-toxic species to prevent chlorine interference rather than sodium arsenite. Test results are measured at 580 nm.

3.0 Interferences

3.1 Chlorine levels above 5 mg/L may interfere. If samples contain more than 5 mg/L chlorine, dilute the sample by a factor that will lower the chlorine level to below 5 mg/L and multiply results by this dilution factor.

3.2 The SPADNS 2 reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 4500F-:I, p 4-82, Standard Methods for the Examination of Waters and Wastewaters, 21st Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS 2 reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference in absorbance in the blank and the sample. A small error in reagent addition is the most prominent source of error in this test.

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.

4.2 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

4.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of any chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in Sections 15.3 and 15.4.

5.0 Equipment

Note: *Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

5.1 Sampling equipment

5.1.1 Sample collection bottles – 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.

5.1.2 Cleaning

6.1.2.1 All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. Preferably, this glassware should be used only for the determination of fluoride and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl is only occasionally required.

6.2 Equipment for sample analysis

6.2.1 Hach Company DR 5000, DR 3800, DR 2800, DR 2700 spectrophotometer or Fluoride Pocket Colorimeter II.

6.3 Equipment for standard preparation

6.3.1 Volumetric flask – Glass, 1000-mL.

6.3.2 Volumetric pipette – Glass, assorted sizes.

7.0 Reagent and Standards

7.1 Reagent water – Water in which fluoride is not detected at or above the method level of this method. Bottled distilled water, or water prepared by passage of tap water through ion exchange and activated carbon have been shown to be acceptable sources of reagent water.

7.2 Hach Company SPADNS 2 Reagent, Cat. No. 2527025, 2947549, 2947553, or 2947517

7.3 Hach Company Fluoride Standard Solutions: 0.5 mg/L as F^- (Cat. No. 40505), 1.5 mg/L as F^- (Cat. No. 40515), 100 mg/L as F^- (Cat. No. 23249).

7.4 Method detection limit solution

7.4.1 Prepare 7 or more replicate MDL solutions by diluting 1.0 mL of the 100 mg/L standard spiking solution (Section 7.3) to 1000 mL. Final concentration = 0.1 mg F^-/L.

7.5 Initial precision and recovery solution

7.5.1 Prepare 4 or more replicate IPR solutions by diluting 10.0 mL of standard spiking solution (Section 7.3) to 1000 mL. Final concentration = 1.0 mg F^-/L.

8.0 Quality Control

8.1 It is recommended that each laboratory that uses this method be required to operate a formal quality assurance program (15.1). The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analyses of laboratory prepared water standards as a test of continued performance to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.
The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the analysis system is in control.

8.1.2 Accompanying QC for the determination of fluoride is required per analytical batch. An analytical batch is a set of samples processed during a contiguous 8-hour period. Each analytical batch must be accompanied

by an ongoing precision and recovery sample, matrix spike sample, and matrix spike duplicate sample resulting in a minimum of four analyses (1 OPR, 1 sample, MS, and MSD).

8.2 Initial demonstration of laboratory capability.

8.2.1 To establish the ability to detect fluoride the analyst shall determine the MDL and ML per the procedure in 40 CFR 136, Appendix B (15.2) using the apparatus, reagents, and standards that will be used in the practice of this method. An achieved MDL and ML less than or equal to the MDL in Section 12.0 is recommended prior to the practice of this method.

8.2.2 Prepare and measure seven replicates of the MDL standard according to the procedure beginning in Section 7.4.1.

8.3 Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.3.1 Prepare and measure four samples of the IPR standard according to the procedure beginning in Section 7.5.

8.3.2 Using the results of the set of four analyses, compute the average percent recovery (x) and the standard deviation of the percent recovery (s) for fluoride. Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

where:

n = Number of samples
x = % recovery in each sample

8.3.2.1 Compare s and x with the corresponding limits for initial precision and recovery in Table 1. If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event correct the problem, and repeat the test.

8.4 Ongoing precision and recovery - To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:

8.4.1 Prepare a precision and recovery standard with each analytical batch.

8.4.1.1 At the end of each analytical batch of samples, analyze a precision and recovery standard. If the recovery is within the acceptable range, measurement process is in control and analysis of samples may proceed. If, however, the recovery is not in the acceptable range, the analytical process is not in control. In this event, correct the problem, re-analyze analytical batch, repeating the ongoing precision and recovery test.

8.4.1.2 The laboratory should add results that pass to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85% to 105%.

8.4.1.3 Depending upon specific program requirements, field replicates may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

9.0 Calibration and Standardization

9.1 The Hach DR series spectrophotometers and Pocket Colorimeter IIs have a built-in calibration that is automatically used when the fluoride program is called up by the user. No further initial calibration is required. However, the instruments have the capability of developing a user-calibration. See manufacturer's manual for instructions.

9.2 Calibration Verification

9.2.1 To verify that the instrument is measuring fluoride properly, analyze a 0.5 mg/L and 1.5 mg/L fluoride standard. Results should be within 15 percent of the actual value.

10.0 Procedure

10.1 Instrument Setup – follow the instrument manufacturer's instructions for instrument setup.

10.2 Preparation

10.2.1 Pipet 10.0 mL of deionized into a dry sample cell. This is the blank.

10.2.2 Pipet 10.0 mL of sample into another dry sample cell. This is the sample.

10.3 Reaction

10.3.1 Carefully pipet 2.0 mL of SPADNS 2 Reagent into each of the sample cells from 10.2.1 and 10.2.2.

10.3.2 React for 1 minute.

10.4 Analysis

10.4.1 Insert the sample cell that contains the blank into the instrument.

10.4.2 Press the "Zero" key on the instrument. The display will show 0.00 mg/L F^-.

10.4.3 Remove the blank. Insert the sample cell that contains the sample into the instrument.

10.4.4 Press the "Read" key on the instrument. The results are in mg/L F^-.

11.0 Data Analysis and Calculations

11.1 Fluoride concentration is calculated automatically against internal instrument calibration.

12.0 Method Performance

Acceptance Criterion	Section	Limit
Method Detection Limit (LIS)	8.2.1	0.04 mg/L F^-
Method Detection Limit (HIS)	8.2.1	0.03 mg/L F^-
Method Limit (LIS)	8.2.1	0.10 mg/L F^-
Method Limit (HIS)	8.2.1	0.10 mg/L F^-
Initial Recovery Range (LIS)	8.31	95% - 105%
Initial Precision (LIS)	8.3.1	0.02
Initial Recovery Range (HIS)	8.31	93% - 113%
Initial Precision (HIS)	8.3.1	0.02

13.0 Pollution Prevention

13.1 Follow guidelines in Section 14.

14.0 Waste Management

14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect air, water, and land by minimizing and control all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

14.2 For further information on waste management, consult "The Waste Management manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 References

15.1 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL-CI, Cincinnati, OH 45268, EPA-600-4-79-019, March 1979.

15.2 40 CFR 136, Appendix B.

15.3 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976)

15.4 "Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.

15.5 Standard Methods for the Examination of Water and Wastewater, p. 4-85 – 4-86 (Method 4500-F D SPADNS) 21st Edition, (2005).

15.6 USEPA Method 340.1

16.0 Tables

16.1 Acceptance Criteria for Performance tests – The QC performance criteria for this method was performed with a Hach Company Fluoride Pocket Colorimeter II and SPADNS 2 Reagent.

Table 1. Initial Precision and Recovery Method Performance

IPR Concentration	Average Recovery (%)		Standard Deviation (%RSD)
1.0 mg/L F^-	LIS	100.0	1.1
	HIS	102.9	2.7

Table 2. Minimum Method Limit Performance

MDL Test Concentration	MDL		ML
0.1 mg/L F^-	LIS	0.041 mg F^-/L	0.10 mg F^-/L
	HIS	0.034 mg F^-/L	0.10 mg F^-/L

17.0 Glossary of Definitions and Purposes

The definitions and purposes are specified to this method but have been conformed to common usage as much as possible.

17.1 Units of weight and measure and their abbreviations

17.1.1 Symbols
°C: degrees Celsius

17.1.2 Alphabetical characters
mg/L: milligram per liter

17.2 Definitions, acronyms, and abbreviations

17.2.1 MDL: Method detection limit

17.2.2 ML: Method limit

17.2.3 IPR: Initial precision and recovery

17.2.4 OPR: On-going precision and recovery

17.2.5 MS: Matrix spike

17.2.6 MSD: Matrix spike duplicate

17.2.7 LIS: Low ionic strength

17.2.8 HIS: High ionic strength

Appendix

	EPA 340.1	SM 4500-F D	Hach Method 10225 (SPADNS 2)
Scope and Application	0.1 - 1.4 mg/L F Drinking, Surface, and Saline Waters, Domestic and Industrial Wastes	0.1 - 1.4 mg/L F	0.1 - 2.00 mg/L F Drinking, Surface, and Saline Waters, Domestic and Industrial Wastes
Summary of Method	The sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl- SPADNS dye is a function of the fluoride concentration.	The sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.	The sample is treated with the SPADNS 2 reagent. The loss of color resulting from the reaction of fluoride with the zirconyl- SPADNS dye is a function of the fluoride concentration. The SPADNS 2 reagent contains a non-toxic species to prevent chlorine interference rather than sodium arsenite.
Equipment	Manual Spectophotometry/Colorimetry	Manual Spectophotometry/Colorimetry	Manual Spectophotometry/Colorimetry
Reagents	Sulfuric Acid Silver Sulfate SPADNS (sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) Zirconyl Chloride Octahydrate Sodium Arsenite	Hydrochloric Acid SPADNS (sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) Zirconyl Chloride Octahydrate Sodium Arsenite	Hydrochloric Acid SPADNS (sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) Zirconium Oxychloride Propietary non-toxic reducing agent
Method Performance	0.83 mg/L F - 97.5% % RSD - 11%	0.83 mg/L F - 98.8% % RSD - 8%	3 Laboratory Average (LIS + HIS) MDL - 0.04 mg/L F ML - 0.12 mg/L F IPR (0.1 mg/L F) - 101% % RSD - 3% DW Matrix % RSD - 1.8%