Hach Company Method 8029 (SPADNS) Spectrophotometric Measurement of Fluoride in Water and Wastewater

Spectrophotometric Measurement of Fluoride in Water and Wastewater

1.0 Scope and Application

1.1 This procedure covers the determination of fluoride in drinking water and domestic and industrial waste waters.

1.2 This method is equivalent to EPA Reference Methods Standard Method 4500-F B/D and ASTM D1179-93, 99(A) for 40 CFR 136 National Pollution Discharge Elimination System (NPDES) monitoring programs and 40 CFR 141 National Primary Drinking Water Regulations (NPDWR) monitoring programs

1.3 This procedure measures fluoride ion (F^-). These forms are defined in Section 4.0.

1.4 The method is applicable in the range from 0.02 to 2.00 mg/L F^-.

2.0 Summary of Method

2.1 The SPADNS for fluoride determination involve the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration.

3.0 Interferences

3.1 This test is sensitive to small amounts of interferences. Glassware must be very clean (acid rins e before each use).

Interfering Substances and Levels

Interfering Substance	Interference Levels and Treatments
Alkalinity (as $CaCO_3$)	At 5000 mg/L it causes a –0.1 mg/L F^- error.
Aluminum	At 0.1 mg/L it causes a –0.1 mg/L F^- error. To check for interferences from aluminum, read the concentration one minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. Waiting 2 hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.
Chloride	At 7000 mg/L it causes a +0.1 mg/L F^- error.
Chlorine	SPADNS 2 Reagent contains non-toxic reductant to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels, dilute sample with deionized water by a factor that will lower chlorine concentration to below 5 mg/L. Perform the procedure, and multiply results by this factor to obtain mg/L Fluoride.
Iron, ferric	At 10 mg/L it causes a –0.1 mg/L F^- error.
Phosphate, ortho	At 16 mg/L it causes a +0.1 mg/L F^- error.
Sodium Hexametaphosphate	At 1.0 mg/L it causes a +0.1 mg/L F^- error.
Sulfate	At 200 mg/L it causes a +0.1 mg/L F^- error.

4.0 Definitions

4.1 The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

4.1.3 Total Fluoride – All fluoride present in the sample, regardless of oxidation state.

5.0 Safety

5.1 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.

5.2 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.

5.3 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 16.6 and 16.7.

6.0 Equipment and Supplies

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.*

6.1 Sampling equipment

6.1.1 Sample collection bottles— Plastic or glass, approximately 1-L, with PTFE-lined screw cap. Note: *In those instances necessitating collection of a smaller aliquot, a smaller sample container may be used.*

6.1.2 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 hexavalent chromium 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 DR 5000, DR 2800, or DR 3800 spectrophotometer.

6.2.2 Variable volume pipette and tips for sample measurement/dispensation.

6.3 Equipment for standard preparation

6.3.1 Volumetric flask – Glass, 1000-mL.

6.3.2 Volumetric flask – Glass, 100-mL.

6.3.3 Volumetric pipette – glass, assorted sizes.

7.0 Reagents 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 Fluoride Reagent Solution or AccuVac® Ampoule test kit (Hach P/N 44449 or Hach P/N 2506025.

7.3 Hach Company Mix Standards

Fluoride Standard Solution, 0.2 mg/L F^-	500 mL	40502
Fluoride Standard Solution, 0.5 mg/L F^-	500 mL	40505
Fluoride Standard Solution, 0.8 mg/L F^-	500 mL	40508
Fluoride Standard Solution, 1.0 mg/L F^-	946 mL	29116
Fluoride Standard Solution, 1.0 mg/L F^-	473 mL	29111
Fluoride Standard Solution, 1.2 mg/L F^-	500 mL	40512
Fluoride Standard Solution, 1.5 mg/L F^-	500 mL	40515
Fluoride Standard Solution, 2.0 mg/L F^-	500 mL	40520
Fluoride Standard Solution, 100 mg/L F^-	500 mL	23249

7.4 Method detection limit solution

7.4.1 Analyze 7 or more replicate 0.2 mg/L F^- standard solution samples.

7.5 Initial precision and recovery (IPR) solution

7.5.1 Analyze 4 or more replicate 1.0 mg/L F^- standard solution samples.

7.6 On-going precision and recovery

7.6.1 Analyze 1 or more replicate 1.0 mg/L F^- standard solution samples.

8.0 Sample Collection Preservation and Storage

8.1 Samples may be stored in glass or plastic bottles for at least seven days when cooled to 4 ^{o} C or lower.

8.2 Warm samples to room temperature before analysis.

9.0 Quality Control

9.1 It is recommended that each laboratory that uses this method be required to operate a formal quality assurance program (Section 16.1). 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.

9.1.1 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 7.5. The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the analysis system is in control. This procedure is described in Sections 7.6.

9.2 Initial demonstration of laboratory capability.

9.2.1 To establish the ability to detect F^-, the analyst shall determine the MDL and ML per the procedure in 40 CFR 136 (Section 16.4) 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 13.0 is recommended prior to the practice of this method.

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

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

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

9.2.3.2 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 chromium (VI). 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

9.2.3.3 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.

9.3 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:

9.3.1 Prepare a precision and recovery standard with each analytical batch according to the procedure beginning in Section 7.6.

9.3.2 At the end of each analytical batch of samples, analyze a precision and recovery standard and compare the concentration recovery with the limits for ongoing precision and recovery in Table 3. If the recovery is in the range specified, measurement process is in control and analysis of samples may proceed. If, however, the recovery is not in the specified 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.

9.3.3 The laboratory should add results that pass the specification in Section 13.0 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%.

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

10.0 Calibration and Standardization

10.1 The Hach Company DR Series colorimeters and spectrophotometers mentioned in Section 6.2 have a built-in calibration that is automatically used when entering the stored procedure number. However, the instruments have the capability of developing a user-calibration. See manufacturer's manual for instructions.

11.0 Procedure

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

11.2 Sample Analysis – Follow the Hach Procedure Document (DOC316.53.01041) for SPADNS chemistry.

12.0 Data Analysis and Calculations

12.1 Fluoride ion (F^-) concentration is calculated automatically against internal instrument calibration.

13.0 Method Performance

Acceptance Criterion	Section	Limit
Method Detection Limit	9.2.1	0.03 mg/L F^-
Minimum Limit	9.2.1	0.02 mg/L F^-
Initial Accuracy	9.2.2	100%
Initial Precision	9.2.2	0.01
On-going Accuracy	User established	

14.0 Pollution Prevention

14.1 Follow guidelines in Section 15.

15.0 Waste Management

15.1 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.

15.2 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.

16.0 References

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

16.2 "Hach Water Analysis Handbook," 5th Edition, (2008).

16.3 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 3-66, Method 3500-Cr B. (1998).

16.4 40 CFR 136, Appendix A, B.

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

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

17.0 Tables

17.1 Acceptance Criteria for Performance tests – The QC performance criteria for this method was performed with a Hach Company DR 5000 spectrophotometer using Hach Method 8029 Kit.

Table 1. Initial Precision and Recovery Method Performance

IPR Concentration	Average Recovery (%)	Standard Deviation (%)
1.0 mg/L F^-	100	0.01

Table 2. Method Detection Limit and Method Limit Performance (Single Laboratory)

MDL Test Concentration	MDL	ML
0.03 mg /L F^-	0.01 mg/L F^-	0.02 mg /L F^-

18.0 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.

18.1 Units of weight and measure and their abbreviations

18.1.1 Symbols
°C: degrees Celsius

18.1.2 Alphabetical characters
mg/L: milligram per liter

18.2 Definitions, acronyms, and abbreviations

18.2.1 MDL: Method detection limit

18.2.2 ML: Minimum limit

18.2.3 IPR: Initial precision and recovery

18.2.4 OPR: On-going precision and recovery

18.2.5 MS: Matrix spike

18.2.6 MSD: Matrix spike duplicate

Fluoride
Method Comparison Tables

	Method 4500-F B/D	Hach 8029/
Scope and Application	0.01 –1.40 mg P/L	0.02 – 2.00 mg P/L
Summary of Method	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 the colorless complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.	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 the colorless complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.
Interference	Chlorine	Chlorine
Equipment	Colorimeter/Spectrophotometer	Colorimeter/Spectrophotometer
Sample Handling/ Preservation	Samples may be stored in glass or plastic bottles for at least seven days when cooled to 4 ^{o} C or lower.	Samples may be stored in glass or plastic bottles for at least seven days when cooled to 4 ^{o} C or lower.
Reagents and Standards	SPADNS Zirconyl-acid Sodium arsenite	**SPADNS Chemistry** SPADNS Zirconyl-acid Sodium arsenite
Method Performance	MDL = 0.01 mg/L F^- Average Recovery of 4 replicates @ 1.00 mg/L F^- = 100% Standard deviation = 0.01 Matrix Spike Recovery: Three drinking water samples spiked at 0.5 mg/L F^- : Average Recovery = 92.2% Standard deviation = 2.7 %RSD = 2.9%	MDL = 0.01 mg/L F^- Average Recovery of 4 replicates @ 1.00 mg/L F^- = 99.8% Standard deviation = 0.01 Matrix Spike Recovery: Three drinking water samples spiked at 0.5 mg/L F^- : Average Recovery = 95.0% Standard deviation = 2.4 %RSD = 2.5%