Hach Method 10312

Spectrophotometric Measurement of Fluoride in Finished Drinking Water Aluminum-Chromeazurol S complex (AL-CAS) Using Planar Reagent-filled Cuvettes

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1.0 Scope and Application

1.1 This method is for the determination of fluoride in finished drinking water.

1.2 The method is applicable in the range from 0.2 to 4.0 mg/L F^-.

1.3 This method is equally effective in performance and use to SM 4500-F^- D for the purposes of regulatory compliance reporting of fluoride.

2.0 Summary of Method

The reagent solution contains an intensely colored aluminum-chromeazurol S complex. The presence of fluoride in the sample removes aluminum from the complex, releasing the free chromeazurol S ion. The free chromeazurol S ion has peak absorbance in a different region of the visible spectrum. The quantifiable change in absorbance is directly proportional to the fluoride concentration. Test results are measured at 427 nm.

3.0 Interferences

3.1 The items listed in the *Interfering Substances* table have been individually checked up to the given concentrations and do not cause interference. The cumulative effects and influence of other ions have not been determined. Sample treatments have been identified to overcome these interferences. Measurement results can be verified using sample dilutions or standard additions.

Interfering substance	Sample treatment
Aluminum	Distillation via SM4500-F^- B
Sulfate above 750 mg/L	Distillation via SM4500-F^- B

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 sheet (MSDS) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in Sections 16.3 and 16.4.

5.0 Sampling 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 – collect samples in new, unused glass or plastic bottles.

6.0 Equipment for Sample Analysis

6.1 Hach Company SL1000 Analyzer (PN 9430000), or equivalent

6.2 Volumetric flasks – Glass Class A: 100 mL and 1000 mL

6.3 Hach Tensette pipet 1-10 mL (PN 1970010), or equivalent

6.3.1 Hach Pipet Tips for Tensette pipet (PN 2558996), or equivalent

6.4 Hach Tensette pipet 0.1-1.0 mL (PN 1970000), or equivalent

6.4.1 Hach Pipet Tips for Tensette pipet (PN 2185628), or equivalent

7.0 Reagents and Standards

7.1 Deionized water – Water in which fluoride ion concentration is below the detection limit of this method. Water prepared by passage of tap water through reverse osmosis and carbon filtration has been shown to be an acceptable source of reagent water.

7.2 Hach Fluoride Chemkey (PN 9878000) or equivalent

7.3 Sodium Fluoride – ACS reagent, ≥99%

7.3.1 Sodium Fluoride Stock Solution - Add 0.2211 g of sodium fluoride (Section 7.3) into a 100 mL volumetric flask (Section 6.2) that contains 50 mL of reagent water (Section 7.1). Dissolve and bring to volume. The final fluoride (F^-) concentration is 1000 mg/L.

7.4 Hach Fluoride Reagent Solution 100 mg/L (PN 23249), or equivalent

7.5 Method Detection Limit (MDL) and Method Limit (ML) Standard Solution

7.5.1 Prepare 7 or more replicate MDL/ML solutions by diluting 2.0 mL of the 100 mg/L standard spiking solution (Section 7.3.1) to 1000 mL of reagent water. Final concentration = 0.20 mg/L F^-.

7.6 Initial Precision and Recovery (IPR) Standard Solution

7.6.1 Prepare 4 or more replicate IPR solutions by diluting 1.0 mL of the 100 mg/L standard spiking solution (Section 7.3.1) to 100 mL of reagent water. Final concentration = 1.0 mg/L F^-.

7.7 Matrix Spike Sample Standard Solution

7.7.1 Prepare 2 or more replicate Matrix Spike samples per sample matrix by adding 0.10 mL of the 1000 mg/L standard spiking solution (Section 7.3.1) to a 100 mL volumetric flask (Section 6.2). Bring to volume with sample matrix. The spike sample matrix concentration is 1.0 mg/L in addition to any background fluoride already present in the sample matrix.

8.0 Sample Collection, Preservation and Storage

8.1 Samples should be collected in fluoride-free polyethylene or glass bottles. Analyze sample within 28 days of collection.

9.0 Quality Control

9.1 Each laboratory that uses this method is expected to operate a formal quality assurance program. 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 Sections 9.2 and 9.3. The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.2 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 (OPR), matrix spike sample (MS), and matrix spike duplicate sample (MSD) resulting in a minimum of four analyses (1 OPR, 1 sample, MS, and MSD).

9.2 Initial demonstration of laboratory capability.

9.2.1 To establish the ability to detect fluoride, the analyst shall determine the MDL and ML 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 and ML in Section 17.1 is recommended prior to the practice of this method.

9.2.2 Prepare and measure seven replicates of the MDL/ML standard (Sect. 7.5) according to the procedure in Section 11.

9.2.3 Using the results of the set of seven analyses, compute the MDL using the following equation:

$$MDL = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}} \times 3.14$$

where:

n = Number of samples (7)
x = measured concentration of each sample

9.2.4 Compute the ML by multiplying the MDL by 3.18 and rounding to the nearest tenth.

9.2.5 Calculate the average percent recovery of the seven MDL replicate results.

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

9.3.1 Prepare and measure four samples of the IPR standard (Sect. 7.6.1) according to the procedure in Section 11.

9.3.2 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 F^-. 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 (4)
x = % recovery in each sample

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9.3.2.1 Compare s and x with the corresponding limits for initial precision and recovery in Table 2 (Sect. 17). 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.

9.4 Ongoing precision and recovery (OPR) - 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:

9.4.1 Prepare a 1.0 mg/L recovery standard with each analytical batch as described in Sect. 7.6.1 and measure according to the procedure in Section 11. Calculate the percent recovery and compare this value with the limits for ongoing recovery in Table 2 (Sect. 17). If the percent recovery meets the acceptance criteria, system performance is acceptable. If the percent recovery falls outside the acceptance criteria, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.1 Measure a matrix sample. After measuring the background concentration, spike the sample with a known concentration of F^- (Sect. 7.7.1). The spike concentration should be within the reporting range of the method. Prepare a duplicate of this spiked sample.

9.4.1.2 Measure the spike duplicates (Sect. 7.7.1) and calculate the spike recovery for each sample and the relative percent difference (RPD) between the two results.

Use the following equation to calculate the spike recovery:

$$Spike\ Recovery = \frac{[Conc] - [Bkgd]}{[Sp]} \times 100$$

where:

[Conc] = the measured concentration of the spiked sample
[Bkgd] = the measured concentration of the un-spiked sample
[Sp] = the concentration of the spike

$$RPD = \frac{|Conc_1 - Conc_2|}{\left(\frac{Conc_1 + Conc_2}{2}\right)} \times 100$$

where:

$Conc_1$ = the concentration of the first spiked sample
$Conc_2$ = the concentration of the second spiked sample

9.4.1.3 Compare the spike recoveries and RPD with the corresponding limits in Table 2 (Sect. 17). If recoveries and RPD meet the acceptance criteria, system performance is acceptable, and analysis of samples may begin. If recoveries or RPD fall outside the limits, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.4 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%. Control charts are acceptable for evaluating process control, but under no circumstances can the control limits be widened beyond those established in the acceptance criteria defined in Section 17.

10.0 Calibration and Standardization

10.1 The Hach SL1000 colorimeter has a built-in calibration that is automatically initiated when the Fluoride procedure is selected through the instrument interface. No further initial calibration is required. However, the instruments have the capability of developing a user-calibration. See manufacturer's manual for instructions.

10.2 Calibration Verification

10.2.1 To verify that the instrument is measuring fluoride properly, analyze a 1.0 mg/L (Sect. 7.6.1) F^- standard. The results should be within 15 percent of the actual value. Perform this calibration verification daily while instrument is in use. If the calibration verification standard result is outside the limit, it is unacceptable. In this event, correct the problem, and repeat the test.

11.0 Procedure

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

11.2 Remove Fluoride Chemkey(s) from packaging and insert into SL1000 instrument

11.3 Fill sample cup to fill line with sample.

11.4 When prompted, dip SL1000 instrument with inserted Fluoride Chemkey(s) into sample cup and remove when prompted (~2 seconds).

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11.5 The automated testing is completed in approximately 7 minutes

11.6 Measurement results will display in mg/L F^-.

12.0 Data Analysis and Calculations

12.1 Fluoride concentration is calculated automatically against internal instrument calibration.

13.0 Method Performance

Performance of the method was demonstrated in multi-lab studies comparing the method against EPA Reference Method SM 4500-Cl G. The method was evaluated in a low ionic strength reference matrix as well as multiple geographically diverse finished drinking water samples obtained from both surface water and ground water sources.

Validation Study Results	Section	Limit
Method Detection Limit	9.2	0.06 mg/L F^-
Method Limit	9.2	0.20 mg/L F^-
Initial Recovery Range	9.3	89.5% - 101%
Initial Precision 95%	9.3	0.02
Matrix Recovery Range	9.4	89.9 – 110%
Matrix Recovery Precision 95%	9.4	0.06

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 40 CFR 136, Appendix B.

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

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

16.4 "Water Analysis Handbook," Hach Company, 8th Edition, 2013.

17.0 Tables

17.1 Acceptance Criteria for Initial Demonstration of Capability and On-going Performance Tests

Table 1. Method Detection Limit and Method Limit Acceptance Criteria

Parameter	Acceptance Criteria
Method Detection Limit	≤ 0.10 mg/L F^-
Method Limit	≤ 0.32 mg/L F^-
Average Method Limit Recovery Range	50 - 150 %

Table 2. Initial Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Relative Standard Deviation	≤ 10%
Percent Recovery Range	85 - 115%

Table 3. Ongoing Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Lab Fortified Blank Recovery	85 - 115%
Sample Matrix Spike Recovery	75 - 125%
Sample Matrix Spike Matrix Spike Duplicate RPD	≤ 10%

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: Method limit

18.2.4 IPR: Initial precision and recovery

18.2.3 OPR: On-going precision and recovery

18.2.4 MS: Matrix spike

18.2.5 MSD: Matrix spike duplicate

18.2.6 RPD: Relative Percent Difference