EPA Office of Water		
New Method Application Form **For Chemical Analytes**		
Applicant Name and Address:	Hach Company 5600 Lindbergh Drive Loveland, Colorado 80538 Attn: Cary B. Jackson 970 669-3050 cjackson@hach.com	EPA Use Only Case No.
Date Application Submitted:	Initial Application: May 13th, 2021; Final Application: August 16, 2022	
Method Number and Title:	Hach Method 10312 – Spectrophotometric Measurement of Fluoride in Finished Drinking Water by Aluminum-Chromeazurol S complex (Al-CAS) using Disposable Planar Reagent-filled Cuvettes	
Analyte(s):	Fluoride	
Type (WW, DW, WW/DW):	DW	
Level of Use: **(LU or NW)**	NW	
Attachments:		
(1) Hach 10312 Validation Study Report (2) Hach 10312 Method (3) Hach 10312 Validation Data (4) Data Collection Certification		

Validation Study Report of Hach Method 10312 for the Determination of Fluoride in Finished Drinking Water Using Planar Reagent-filled Cuvettes

Submitted by:

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## Background

Identity of New Method

The new method is identified as Hach Method 10312 Fluoride using Chromeazurol S chemistry with Planar reagent-filled cuvettes.

Analyte – Fluoride
CAS No. – 16984-48-8

Method Summary

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. Temperature is controlled to increase the rate of reaction and improve reproducibility.

violet-colored Aluminum-Chromeazurol S complex   red-colored Chromeazurol S ion
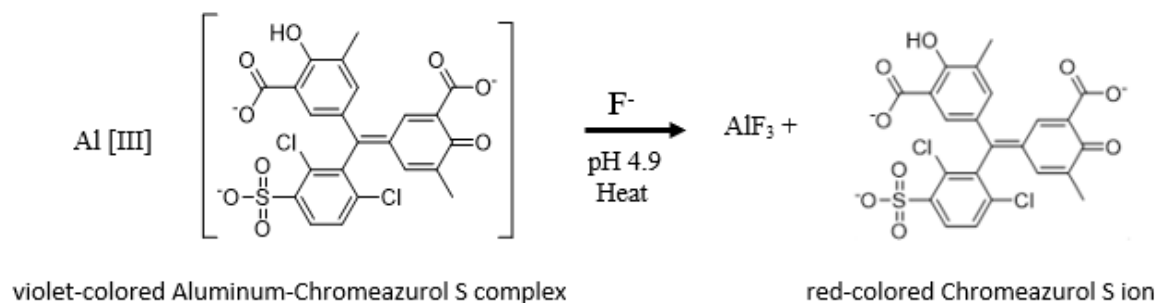
Justification and Reasons for Development

The colorimetric EPA reference method for measurement of fluoride (SM4500-F⁻ D) uses a solution of zirconium 1,8-Dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt (SPADNS) with pH less than 2 that is hazardous and corrosive. SPADNS chemistry requires sodium arsenite to mitigate chlorine interference. Current non-colorimetric EPA reference methods for the measurement of fluoride (EPA Methods 300.0 and 300.1, SM4500-F⁻ C and E, SM4140 B, SM4110 B and C, ASTM D1179-16(B), ASTM D4327-17, and ASTM D6508-15) are costly and inconvenient. The proposed "green" chemistry method is cost effective, excludes the use of toxic metals and corrosive solutions, expands the colorimetric calibration range up to 4 mg/L F⁻, reduces sulfate interference, and is equally effective in performance to that of the EPA Reference Method SM 4500-F D.

Purpose of Study

The purpose of this study is to evaluate the proposed Hach Method 10312 (against the USEPA reference fluoride method (SM4500-F D) for approval and use in USEPA regulatory drinking water programs.

Program Use

The scope of this method is for use in water programs where fluoride is determined in drinking water matrices.

The intended matrix for this method is finished drinking water. The measurement range is from 0.20 to 4.0 mg F⁻ /L.

Study Implementation

Study Sponsor

The organizational sponsor responsible for managing this study is Hach.

Study Participants

The participants, laboratories, and test matrices were selected from geographically diverse regions of the United States and are listed in the Table 1.

Table 1. Matrix Participants, Laboratories, Test Matrices

Matrix Facility	Laboratory	Source of Treated Test Water
City of Loveland, Colorado	Hach	Surface Water
City of Fort Collins, Colorado	ALS Laboratories	Surface Water
City of Lafyette, Louisiana	Element Testing	Ground Water

Study Schedule

The study was conducted from October 7, 2021 to December 7, 2021. Samples were collected and analyzed at each testing facility on October 7, 2021, November 15, 2021, and December 7, 2021. Collection of samples followed standard USEPA sampling procedures found in 40 CFR 141.23.

Analysis Description

The number and types of analyses performed by each laboratory are described in Table 2:

Table 2. Description of Analyses for Each Matrix by Each Laboratory

Analysis	Number of Tests	Total Validation Tests
Method Detection Limit/Method Limit – Low Ionic Strength Water	7	21
Method Detection Limit/Method Limit – High Ionic Strength Water*	7	21
Initial Precision and Accuracy – Low Ionic Strength Water	4	12
Initial Precision and Accuracy – High Ionic Strength Water*	4	12
Matrix Sample	1	3
Matrix Spike Sample	1	3
Matrix Spike Duplicate Sample	1	3

*High Ionic Strength Water (HISW) was made by adding 1.40 g of NaHCO3, 1.48 g of Na2SO4, and 1.54 g of NaCl to a 1 liter of Deionized water

Calculations, Data Analysis and Discussion

Test data and statistical calculations for each laboratory and matrix and pooled statistics is provided in Hach Validation Data and Statistics spreadsheet (Hach Method 10312 Validation Data and Statistics.xlsx). Summary of statistical for each of the three drinking water matrices are listed in Tables 1-3 below.

Sulfate ions are known to cause a positive interference for both SM 4500-F D as well as Hach Method 10312. However, Hach's Method 10312 can mitigate higher concentrations before being notably affected by sulfate ions. SM 4500-F D has a 0.10 mg/L positive interference with ~200 mg/L sulfate. Hach's Method 10312 can handle up to 750 mg/L Sulfate (more than 3x SM 4500-F D) before resulting in a high bias 0.10 mg/L F. This explains the high bias in High Ionic Strength Water (HISW) for both methods below.

Table 1. City of Loveland Water Plant **(Hach)**

Test Matrix	SM 4500-F⁻ D				Hach Method 10312			
	MDL (mg/L)	*ML (mg/L)*	*Average % Recovery*	*Standard Deviation of % Recovery*	*MDL (mg/L)*	*ML (mg/L)*	*Average % Recovery*	*Standard Deviation of % Recovery*
Low Ionic Strength Reagent Water	0.08	0.26	102	12	0.07	0.22	92.9	10
High Ionic Strength Reagent Water	0.07	0.24	402	12	0.05	0.17	187	8.6
Test Matrix	*Initial Precision and Recovery*			*Initial Precision and Recovery*				
	Average % Recovery	*% Bias*	*%Standard Deviation*	*Average % Recovery*	*% Bias*	*% Standard Deviation*		
Low Ionic Strength Reagent Water	103	3.0	3.6	99.5	0.5	1.9		
High Ionic Strength Reagent Water	133	33	4.4	114	14	1.4		
Test Matrix	*Matrix Spike/Matrix Spike Duplicate Analysis*			*Matrix Spike/Matrix Spike Duplicate Analysis*				
	Average % Recovery	*Relative % Difference)*	*%Standard Deviation*	*Average % Recovery*	*Relative % Difference)*	*%Standard Deviation*		
Hach Tap Water	92.0	13.0	8.5	99.0	2.0	1.4		

Table 2. City of Fort Collins Water Plant (ALS Laboratories)

Test Matrix	SM 4500-F⁻ D				Hach Method 10312			
	MDL (mg/L)	ML (mg/L)	Average % Recovery	Standard Deviation of % Recovery	MDL (mg/L)	ML (mg/L)	Average % Recovery	Standard Deviation of % Recovery
Low Ionic Strength Reagent Water	0.07	0.21	154	9.8	0.06	0.19	93.6	8.8
High Ionic Strength Reagent Water	0.07	0.22	402	11	0.07	0.21	149	11
Test Matrix	Initial Precision and Recovery			Initial Precision and Recovery				
	Average % Recovery	% Bias	%Standard Deviation	Average % Recovery	% Bias	% Standard Deviation		
Low Ionic Strength Reagent Water	110	10	0.5	97.8	2.2	3.4		
High Ionic Strength Reagent Water	142	42	4.2	114	14	1.0		
Test Matrix	Matrix Spike/Matrix Spike Duplicate Analysis			Matrix Spike/Matrix Spike Duplicate Analysis				
	Average % Recovery	Relative % Difference)	%Standard Deviation	Average % Recovery	Relative % Difference)	%Standard Deviation		
Hach Tap Water	96.0	4.2	2.8	105	9.5	7.1		

Table 3. City of Lafyette Water Plant (Element Testing)

Test Matrix	SM 4500-F⁻ D				Hach Method 10312			
	MDL (mg/L)	ML (mg/L)	Average % Recovery	Standard Deviation of % Recovery	MDL (mg/L)	ML (mg/L)	Average % Recovery	Standard Deviation of % Recovery
Low Ionic Strength Reagent Water	0.11	0.36	88.6	17	0.08	0.25	101	12
High Ionic Strength Reagent Water	0.12	0.38	357	19	0.06	0.20	165	10
Test Matrix	Initial Precision and Recovery				Initial Precision and Recovery			
	Average % Recovery	% Bias		%Standard Deviation	Average % Recovery	% Bias		% Standard Deviation
Low Ionic Strength Reagent Water	95.8	4.2		1.3	100	0		2.2
High Ionic Strength Reagent Water	133	33		4.0	115	15		1.0
Test Matrix	Matrix Spike/Matrix Spike Duplicate Analysis				Matrix Spike/Matrix Spike Duplicate Analysis			
	Average % Recovery	Relative % Difference)		%Standard Deviation	Average % Recovery	Relative % Difference)		%Standard Deviation
City of Lafyette Tap Water	119	8.4		7.1	110	11		8.5

Pooled Performance Statistics

The pooled statistics for method detection limit (MDL) and minimum limit (ML), initial precision and recovery (IPR), and matrix spike recovery followed the criteria detailed in Appendix D, Tier 2 of Section 9 of the Guidance Document for EPA approval of new methods[1]. A summary of the pooled quality control acceptance criteria is described in Table 4.

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[1] Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water, March 1999 EPA-821-98-003

Table 4: Pooled Performance Statistics

Test Matrix	SM 4500-F⁻ D				Hach Method 10312			
	Method Detection Limit (MDL) mg/L	Rounded Minimum Limit (ML) mg/L	Average % Recovery	Standard Deviation of % Recovery	Method Detection Limit (MDL) mg/L	Rounded Minimum Limit (ML) mg/L	Average % Recovery	Standard Deviation of % Recovery
Low Ionic Strength Water	0.07	0.20	115	32	0.06	0.20	95.7	0.02
High Ionic Strength Water	0.07	0.20	387	26	0.05	0.20	167	18

Test Matrix	Initial Precision and Recovery (IPR)					Initial Precision and Recovery (IPR)				
	Average Percent (%) Recovery	Percent (%) Bias	Lower Limit of (%) Recovery	Upper Limit of % Recovery	Precision 95% Confidence	Average Percent (%) Recovery	Percent (%) Bias	Lower Limit of (%) Recovery	Upper Limit of % Recovery	Precision 95% Confidence
Low Ionic Strength Water	103	2.9	76.1	130	4.1	99.1	0.9	94.7	104	4.5
High Ionic Strength Water	136	36.0	116	156	10.1	115	14.5	112	117	2.3

Test Matrix	Matrix Spike Recovery					Matrix Spike Recovery				
	Average Percent (%) Recovery	Percent (%) Bias	Lower Limit of (%) Recovery	Upper Limit of % Recovery	RSD_{max} %	Average Percent (%) Recovery	Percent (%) Bias	Lower Limit of (%) Recovery	Upper Limit of % Recovery	RSD_{max} %
Drinking Water	102	2.3	56.9	148	29	105	4.7	84.3	125	28

Data Analysis/Discussion

MDL Results

The low ionic strength matrix MDL results for each of the three test facilities ranged from 0.07 mg/L to 0.11 mg/L for EPA Reference Method SM 4500-F D and 0.06 mg/L to 0.08 mg/L for Hach Method 10312. The high ionic strength matrix MDL results for each of the three facilities ranged from 0.07 mg/L to 0.12 mg/L for EPA Reference Method SM 4500-F D and 0.05 mg/L to 0.07 mg/L for Hach Method 10312

The low ionic strength matrix percent recovery from the MDL spike results for each of the three test facilities ranged from 88.6% to 154% for EPA Reference Method SM 4500-F D and 92.9% to 101% for Hach Method 10312. The high ionic strength matrix percent recovery from the MDL spike results for each of the three test facilities ranged from 357% to 402% for EPA Reference Method SM 4500-F D and 149% to 187% for Hach Method 10312.

The pooled low ionic strength matrix paired MDL/rounded ML results for EPA Reference SM 4500-F D and Hach Method 10312 were determined to be 0.07/0.20 mg/L and 0.06/0.20 mg/L, respectively. The pooled high ionic strength matrix paired MDL/rounded ML results for EPA Reference SM 4500-F D and Hach Method 10312 were determined to be 0.07/0.20 mg/L and 0.05/0.20 mg/L, respectively.

The pooled low ionic strength matrix MDL test average % recovery/standard deviation for EPA Reference SM 4500-F D and Hach Method 10312 were determined to be 115%/32% and 95.7%/0.2% respectively. The pooled high ionic strength matrix MDL test average % recovery/standard deviation for EPA Reference SM 4500-F D and Hach Method 10312 were determined to be 387%/26% and 167%/18%, respectively.

Initial Precision and Recovery Results

The IPR average recovery results for low ionic strength reagent water from each of the three facilities ranged from 95.8% to 110% for EPA Reference Method SM 4500-F D and 97.8% to 100% mg/L for Hach Method 10312. The IPR average recovery results for high ionic strength reagent water from each of the three facilities ranged from ranged from 133% to 142% for EPA Reference Method SM 4500-F D, and 114% to 115% for Hach Method 10312.

The pooled low ionic strength reagent water recovery results for EPA Reference Method SM 4500-F D ranged from 76.1% to 130%, with a 95% precision of 4.1%, and 94.7% to 104% with a 95% precision of 4.5% for Hach Method 10312. The pooled high ionic strength reagent water recovery results for EPA Reference Method SM 4500-F D resulted in 116% to 156% with a 95% precision of 10.1%, and 112% to 117% with a 95% precision of 2.3% for Hach Method 10312.

Matrix Spike Results

The average matrix spike recovery results of the three facilities ranged from 92.0% to 119% for EPA Reference Method SM 4500-F D and 99.0% to 110% for Hach method 10312. The standard deviation for matrix spike recoveries ranged from 2.8 to 8.5 for EPA Reference Method SM 4500-F D and 1.4 to 8.5 for Hach Method 10312.

The pooled matrix spike results of recovery ranged from 56.9% to 148% for EPA Reference Method SM 4500-F D and 84.3% to 125% for Hach Method 10312. The % RSD max precision results for the EPA Reference Method SM 4500-F D and Hach Method 10312 were determined to be 29% and 29%, respectively.

Validation Study Conclusion

A validation study was conducted to compare the performance of Hach Method 10312 for the measurement of copper in water to that of the EPA Reference Method SM 4500-F D. The results from this study indicate that Hach Method 10312 is equally effective to that of the EPA Reference Method SM 4500-F D for Safe Drinking Water Act monitoring and compliance reporting programs.

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

Acceptance criteria for Initial Demonstration of Capability and On-going Performance tests of Hach Method 10312 have been determined[2] based on the discussions from EPA Office of Ground Water and Drinking Water and the validation performance results of the EPA Reference Method SM4500-F D.

Method Detection Limit and Method Limit Acceptance Criteria

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

Initial Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Relative Standard Deviation	$\leq$ 10%
Percent Recovery Range	85 – 115%

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	$\leq$ 10%

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[2] Hach Company Method 10312 Revision 1.0, August 2022