

Office of Ground Water and Drinking Water
May 9, 2023

MEMORANDUM

SUBJECT: Basis for Expedited Approval of Hach Method 10312: Spectrophotometric Measurement of Fluoride in Finished Drinking Water Aluminum-Chromeazurol S complex (AL-CAS) Using Planar Reagent-filled Cuvettes

FROM: William A. Adams, Chemist,
SRMD/TSB

TO: The Record

Hach Company's method for the analysis of fluoride in drinking water using Chromeazurol chemistry with planar filled cuvettes was submitted as an alternate test procedure to Standard Methods 4500-F D (SM 4500-F D), Fluoride SPADNS Method. SM 4500-F D is approved in the national primary drinking water regulations at 40 CFR 141.23(k)(1) for the determination of fluoride.

Hach Method 10312 uses a reagent solution that 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 (427 nm) that is measured using a colorimeter. The quantifiable change in absorbance is directly proportional to the fluoride concentration. Temperature is controlled to increase the rate of reaction and improve reproducibility. This method improves upon SM 4500-F D through excluding the use of toxic metals and corrosive solutions, expanding the calibration range, and reducing sulfate interferences. Hach Method 10312 is also less costly and more convenient than current non-colorimetric EPA approved methods.

A multi-site validation study was conducted to compare the performance of Hach Method 10312 with SM 4500-F D, one of the approved methods for the analysis of fluoride in drinking water. There were three facilities and laboratories used in the study, with two facilities using a surface source drinking water and one using a ground source drinking water. Method detection limits and method limits, precision and accuracy performance in high and low ionic strength water, and matrix spike studies were used for direct Hach Method 10312 and SM 4500-F D comparability. The complete data summary is provided in the Hach Method 10312 ATP Validation Study Report. Briefly, the results are as follows:

- 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. The high bias was attributed to the presence of high levels of sulfate in the matrixes.
- 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.
- 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.

Based on the results of the validations study, Hach Method 10312 was determined to be equally as effective as the reference SM 4500-F D in determining fluoride in drinking water.