Fluoride

DOC316.53.01184

USEPA SPADNS 2 Method[1] **Method 10225**

0.02 to 2.00 mg/L F^- **Reagent Solution or AccuVac® Ampuls**

Scope and application: For water, wastewater and seawater; USEPA accepted for reporting for drinking and wastewater analyses (distillation required).[2]

[1] Adapted from Standard Methods for the Examination of Water and Wastewater, 4500-F B & D.
[2] Procedure is equivalent to USEPA Method 340.1 for drinking water and wastewater.

Test preparation

Instrument-specific information

Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests. Table 2 shows sample cell and adapter requirements for AccuVac Ampul tests. The tables also show all of the instruments that have the program for this test.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for reagent addition

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The fill line is toward the user.	2401906 

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter
DR 6000 DR 5000 DR 900	—
DR 3900	LZV846 (A)
DR 3800 DR 2800 DR 2700	LZV584 (C)
DR 1900	9609900 or 9609800 (C)

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
The sample and deionized water must be at the same temperature (±1 °C). Temperature adjustments can be made before or after the reagent addition.
Measure the volume of the reagent accurately. Use a volumetric or high precision pipet if possible.
If the test result is over-range, dilute a fresh sample with a known volume of deionized water and do the test again. Multiply the result by the dilution factor.
Minor variations between lots of reagent become measurable above 1.5 mg/L. While results above 1.5 mg/L are usable for most purposes, for the best accuracy dilute the sample to a lower concentration.
The SPADNS 2 Reagent contains a non-toxic reducing agent to prevent chlorine interference. SPADNS 2 Reagent does not contain sodium arsenite.
The reagent that is used in this test is corrosive. Use protection for eyes and skin and be prepared to flush any spills with running water.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Reagent solution test

Description	Quantity
Pipet filler, safety bulb	1
Pipet, volumetric, Class A, 2.00-mL	1
Pipet, volumetric, Class A, 10.00-mL	1
SPADNS 2 Reagent Solution	4 mL
Thermometer	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific table PPAV.)	2
Water, deionized	10 mL

Refer to Consumable and replacement items on page 6 for order information.

AccuVac Ampuls

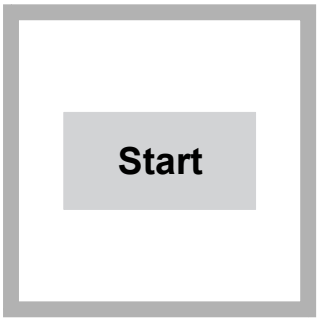
Description	Quantity
Beaker, 50-mL	1
SPADNS 2 Fluoride Reagent AccuVac® Ampuls	1
Stoppers, for 18-mm tubes and AccuVac Ampuls	2
Water, deionized	40 mL

Refer to Consumable and replacement items on page 6 for order information.

Sample collection and storage

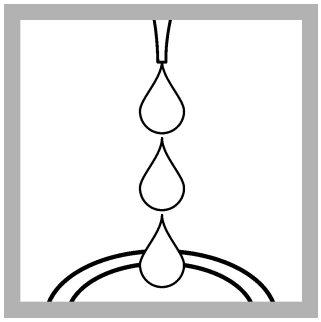
- Collect samples in clean glass or plastic bottles.
- Samples can be kept for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

Reagent solution test

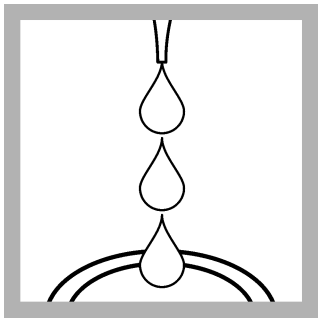


1. Start program **190 Fluoride**. For information about sample cells, adapters or light shields, refer to Instrument-specific table PPAV.

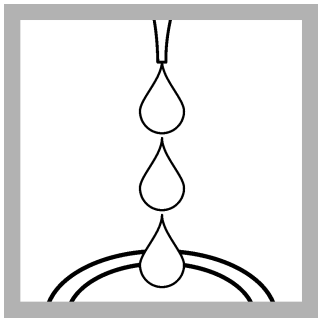
Note: *Although the program name can be different between instruments, the program number does not change.*



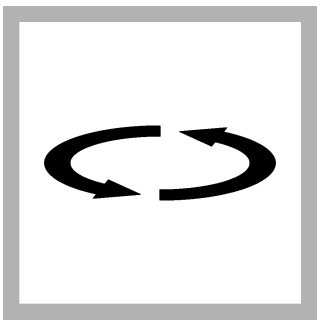
2. Prepare the sample: Use a pipet to add 10.0 mL of sample to a dry sample cell.



3. Prepare the blank: Use a pipet to add 10.0 mL of deionized water to a dry sample cell.

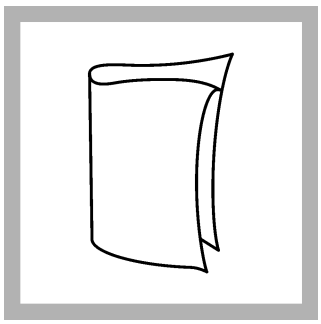


4. Use a pipet to add 2.0 mL of SPADNS 2 reagent to each cell.

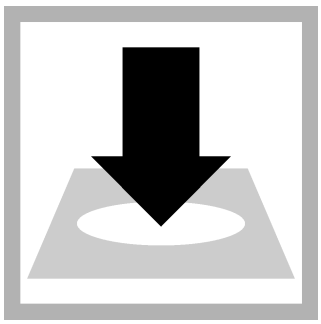


5. Swirl to mix.

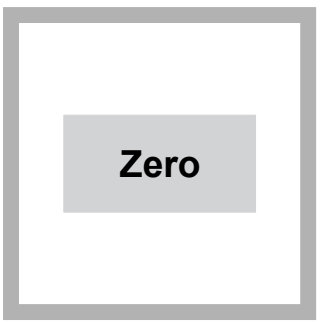
6. Start the instrument timer. A 1-minute reaction time starts.



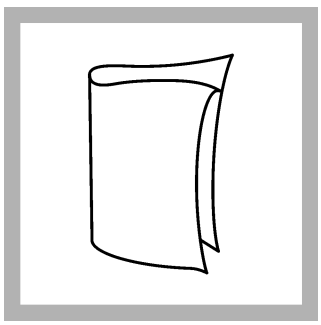
7. When the timer expires, clean the blank sample cell.



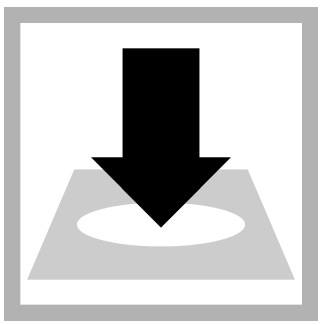
8. Insert the blank into the cell holder.



9. Push **ZERO**. The display shows 0.00 mg/L F^-.



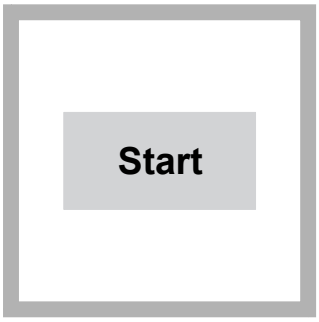
10. Clean the prepared sample cell.



11. Insert the prepared sample into the cell holder.

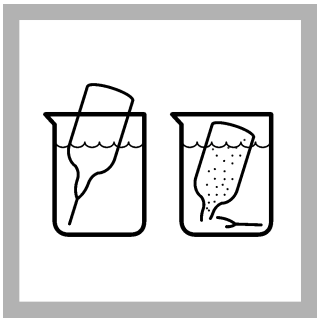
12. Push **READ**. Results show in mg/L F^-.

AccuVac Ampul test

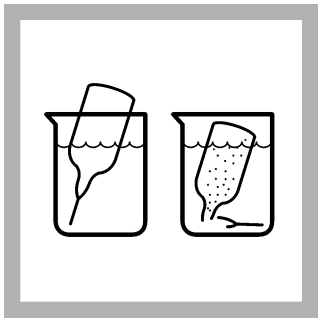


1. Start program **195 Fluoride AV**. For information about sample cells, adapters or light shields, refer to Instrument-specific table PPAV.

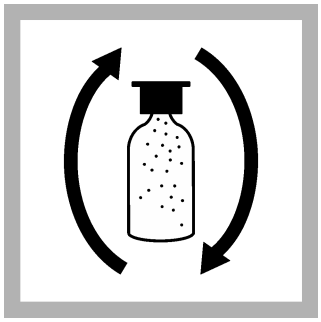
Note: *Although the program name can be different between instruments, the program number does not change.*



2. Prepare the sample: Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the AccuVac Ampul fills completely.

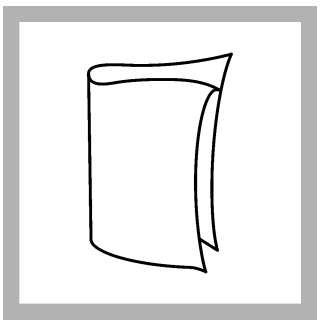


3. Prepare the blank: Pour at least 40 mL of deionized water into a 50-mL beaker. Fill an AccuVac Ampul with deionized water. Keep the tip immersed while the AccuVac Ampul fills completely.

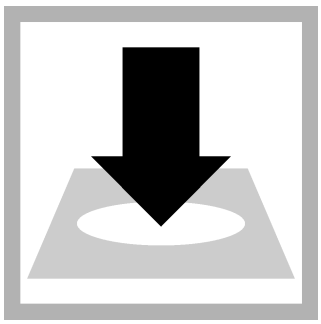


4. Quickly invert the AccuVac Ampuls several times to mix.

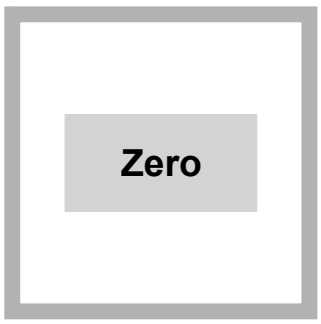
5. Start the instrument timer. A 1-minute reaction time starts.



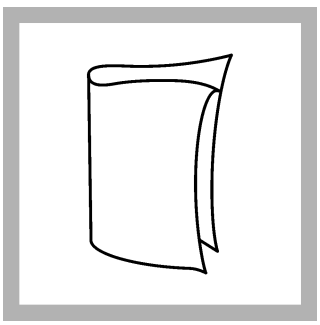
6. When the timer expires, clean the blank AccuVac Ampul.



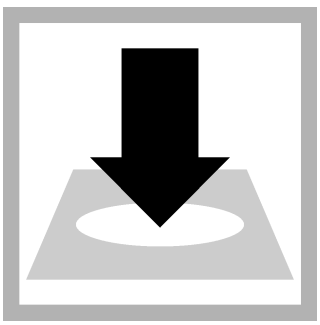
7. Insert the blank AccuVac Ampul into the cell holder.



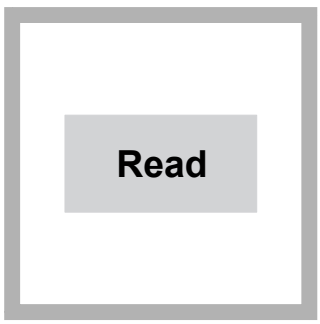
8. Push **ZERO**. The display shows 0.00 mg/L F^-.



9. Clean the AccuVac Ampul.



10. Insert the prepared sample AccuVac Ampul into the cell holder.



11. Push **READ**. Results show in mg/L F^-.

Interferences

This test is sensitive to small amounts of contamination. Glassware must be very clean (acid rinse before each use). Repeat the test with the same glassware to make sure that the results are accurate.

Interfering substance	Interference level
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 find whether there is an aluminum interference, read the concentration 1 minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. To remove the effect of up to 3.0 mg/L aluminum, wait 2 hours, then take the final reading.
Chloride	At 7000 mg/L, it causes a +0.1 mg/L F^- error.
Chlorine	SPADNS 2 Reagent contains enough non-toxic reductant to remove interference of up to 5 mg/L chlorine. For higher chlorine levels: **1.** Dilute the sample with deionized water by a factor that will lower the chlorine concentration to below 5 mg/L. **2.** Use the test procedure to measure the fluoride concentration. **3.** Multiply the result by the dilution factor to get 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.

Distillation

To eliminate most interferences, distill the sample, then use the distilled sample in the test procedure.

Prerequisite—prepare the distillation solution:

1. Measure 60 mL of deionized water into a 250-mL, glass Erlenmeyer flask.
2. With constant stirring, add 120 mL of concentrated sulfuric acid. **Caution: The mixture will become very hot. Put the flask in an ice bath to decrease the temperature of the solution.**

Distillation procedure:

1. Set up the distillation apparatus for general purpose distillation. Refer to the Distillation Apparatus manual for proper assembly.
2. Set up a 125-mL Erlenmeyer flask to collect the distillate.
3. Turn on the water and adjust to maintain a steady flow through the condenser.
4. Use a 100-mL graduated cylinder to add 100 mL of sample into the distillation flask.
5. Add a magnetic stir bar and 5 glass beads.
6. Set the stirrer power to on. Set the stir control to 5.
7. Use a 250-mL graduated cylinder to carefully add 150 mL of distillation solution into the flask.

   Note: *For samples with large amounts of chloride, add 5 mg of silver sulfate to the sample for every mg/L of chloride in the sample.*
8. With the thermometer inserted, set the heat control to 10. The yellow pilot lamp is an indication that the heater is on.
9. When the temperature is 180 °C (356 °F) or when 100 mL of distillate has been collected, turn the still off (takes about 1 hour).
10. Dilute the distillate to a volume of 100 mL, if necessary. Use the diluted distillate in the test procedure.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Standard solution within the test range.

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
190	1.00 mg/L F^-	0.97–1.03 mg/L F^-	0.024 mg/L F^- at 1 mg/L
195	1.00 mg/L F^-	0.92–1.08 mg/L F^-	0.03 mg/L F^- at 1 mg/L

Summary of method

The SPADNS 2 Method for fluoride determination involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex that bleaches the red color in an amount proportional to the fluoride concentration. This method is equivalent to the EPA method for NPDES and NPDWR reporting purposes when the samples have been distilled. Seawater and wastewater samples require distillation. The measurement wavelength is 580 nm for spectrophotometers or 610 nm for colorimeters.

Consumable and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
SPADNS 2 Reagent Solution	4 mL	500 mL	2947549
OR			
SPADNS 2 Fluoride Reagent AccuVac® Ampuls	2	25/pkg	2527025
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/Test	Unit	Item no.
Pipet filler, safety bulb	1	each	1465100
Pipet, volumetric, Class A, 2.00-mL	1	each	1451536
Pipet, volumetric, Class A, 10.00-mL	1	each	1451538
Thermometer	1	each	2635700
Beaker, 50-mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards

Description	Unit	Item no.
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^-	1000 mL	29153
Fluoride Standard Solution, 1.0-mg/L F^-	500 mL	29149
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
Drinking Water Standard, Mixed Parameter, Inorganic for F^-, NO_3–N, PO_4^{3-}, SO_4^{2-}	500 mL	2833049

Distillation reagents and apparatus

Description	Unit	Item no.
Graduated cylinder, 100-mL	each	50842
Graduated cylinder, 250-mL	each	50846
Distillation apparatus set, general purpose	each	2265300
Distillation heater and support for apparatus set, 115 VAC option	each	2274400
Distillation heater and support for apparatus set, 230 VAC option	each	2274402
Flask, Erlenmeyer, 125-mL	each	2089743
Flask, Erlenmeyer, 250-mL	each	50546
Glass beads	100/pkg	259600
Stir bar, magnetic	each	1076416
Sulfuric Acid, ACS	500 mL	97949

Optional reagents and apparatus

Description	Unit	Item no.
Silver Sulfate	113 g	33414
Balance, analytical, 80 g x 0.1 mg 100–240 VAC	each	2936701
Paper, for weighing, 100 x 100 mm	500/pkg	1473885

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

01/2014, Edition 9