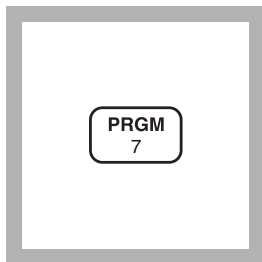


FLUORIDE (0 to 2.00 mg/L F⁻)

For water, wastewater and seawater

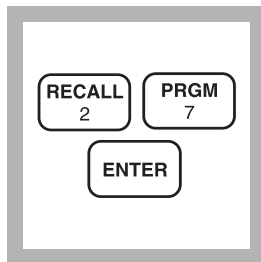
SPADNS Method* (Reagent Solution or AccuVac Ampuls)**Using SPADNS Reagent Solution**

1. Enter the stored program number for fluoride (F) powder pillows.

Press: **PRGM**

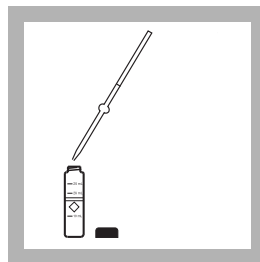
The display will show:

PRGM ?

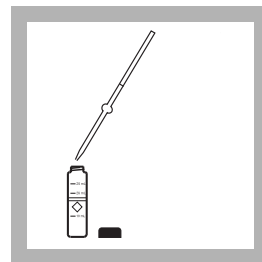


2. Press: **27 ENTER**

The display will show **mg/L, F** and the **ZERO** icon.

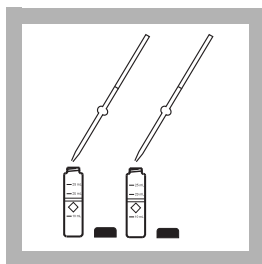


3. Pipet 10.0 mL of sample into a dry 10-mL sample cell (the prepared sample).



4. Measure 10.0 mL of deionized water into a second dry sample cell (the blank).

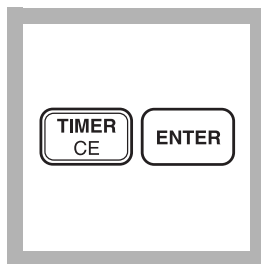
Note: The sample and blank should be at the same temperature (± 1 °C). Temperature adjustments may be made before or after reagent addition.



5. Pipet 2.00 mL of SPADNS Reagent into each cell. Swirl to mix.

Note: SPADNS Reagent is toxic and corrosive; use care while measuring. Use a pipet filler.

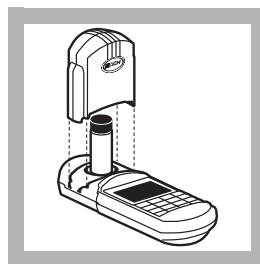
Note: The SPADNS Reagent must be measured accurately.



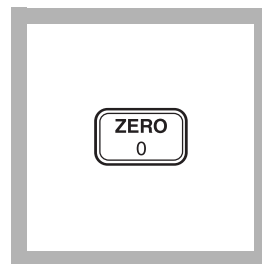
6. Press:

TIMER ENTER

A one minute reaction period will begin.



7. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

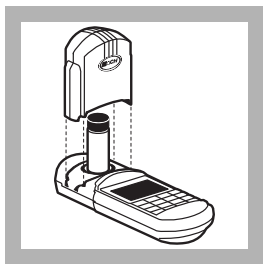


8. Press: **ZERO**

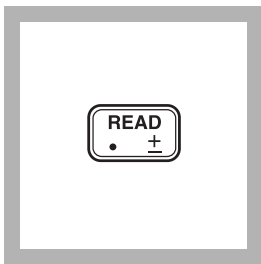
The cursor will move to the right, then the display will show:

0.00 mg/L F

* Adapted from *Standard Methods for the Examination of Water and Wastewater*. The procedure for this instrument uses an alternate wavelength outside the accepted 550-580 nm range. The reagents used are the same as those in the USEPA accepted method.



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

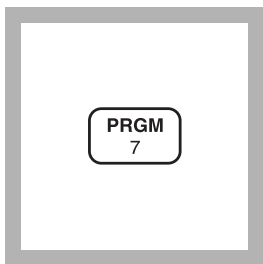


10. Press: **READ**

The cursor will move to the right, then the result in mg/L fluoride will be displayed.

***Note:** Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check following these steps.*

Using AccuVac Ampuls

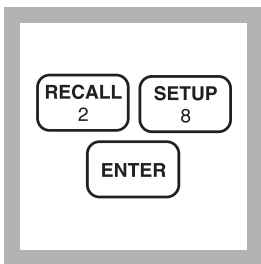


1. Enter the stored program number for fluoride (F⁻)- AccuVac Ampuls.

Press: **PRGM**

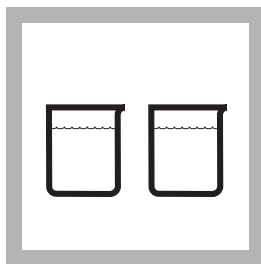
The display will show:

PRGM ?

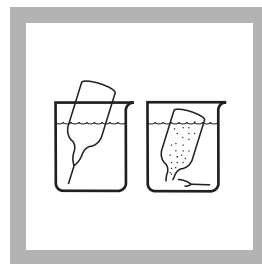


2. Press: **28 ENTER**

The display will show **mg/L, F** and the **ZERO** icon.

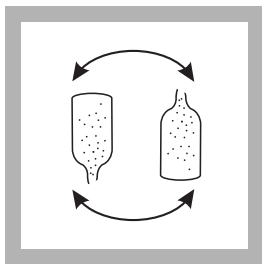


3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second beaker.



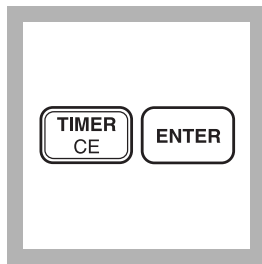
4. Fill a SPADNS Fluoride Reagent AccuVac Ampul with sample by breaking the tip on the bottom of the beaker. Fill a second AccuVac Ampul with deionized water (the blank).

***Note:** Keep the tip immersed while the ampule fills completely.*



5. Quickly invert the ampules several times to mix. Wipe off any liquid or fingerprints.

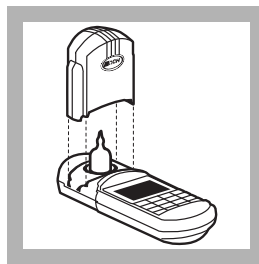
Note: Do not place finger over the broken tip- the liquid will remain in the ampul.



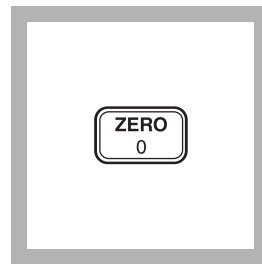
6. Press:

TIMER ENTER

A one-minute reaction period will begin.



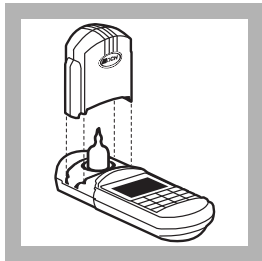
7. After the timer beeps place the blank into the cell holder. Tightly cover the ampule with the instrument cap.



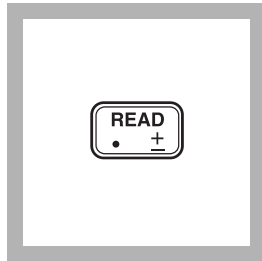
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L F



9. Place the AccuVac Ampul containing the sample into the instrument. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L fluoride will be displayed.

Note: Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check following these steps.

FLUORIDE, continued

Sampling and Storage

Collect samples in plastic bottles. Samples may be stored up to 28 days.

Accuracy Check

Standard Solution Method

A variety of standard solutions covering the entire range of the test are available from Hach. Use these in place of sample to verify technique. Minor variations between lots of reagent become measurable above

1.5 mg/L. While results in this region are usable for most purposes, better accuracy may be obtained by diluting a fresh sample 1:1 with deionized water and retesting. Multiply the result by 2.

Standard Adjust

To adjust the calibration curve using the reading obtained with a 1.80-mg/L Standard Solution, press **SETUP** and use the arrow keys to scroll to the “STD” setup option. Press **ENTER** to activate the option. Then enter **1.80** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Standard Curve Adjustment* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory, using standard solutions of 1.00 mg/L fluoride and two lots of SPADNS Reagent with the instrument, a single operator obtained standard deviations of ± 0.035 mg/L fluoride.

In a single laboratory, using standard solutions of 1.00 mg/L fluoride and two lots of SPADNS AccuVac Reagent with the instrument, a single operator obtained standard deviations of ± 0.040 mg/L fluoride.

Estimated Detection Limit (EDL)

The EDL for programs 27 and 28 is 0.05 mg/L F⁻. For more information on derivation and use of Hach’s estimated detection limit, see *Section 1*.

Interferences

This test is sensitive to small amounts of interference. Glassware must be very clean. Repeating the test with the same glassware is recommended to ensure that results are accurate.

The following substances interfere to the extent shown:

Substance	Concentration	Error
Alkalinity (as CaCO ₃)	5000 mg/L	-0.1 mg/L F ⁻
Aluminum	0.1 mg/L	-0.1 mg/L F ⁻
Chloride	7000 mg/L	+0.1 mg/L F ⁻
Iron, ferric	10 mg/L	-0.1 mg/L F ⁻
Phosphate, ortho	16 mg/L	+0.1 mg/L F ⁻
Sodium Hexametaphosphate	1.0 mg/L	+0.1 mg/L F ⁻
Sulfate	200 mg/L	+0.1 mg/L F ⁻

SPADNS Reagent contains enough arsenite to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels, add one drop of Sodium Arsenite Solution to 25 mL of sample for each 2 mg/L of chlorine.

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 two hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.

Most interferences can be eliminated by distilling the sample from an acid solution as described below:

- a) Set up the distillation apparatus for the general purpose distillation. See the Hach Distillation Apparatus Manual. Turn on the water and make certain it is flowing through the condenser.
- b) Measure 100 mL of sample into the distillation flask. Add a magnetic stirring bar and turn on the heater power switch. Turn the stir control to 5.
- c) Cautiously measure 150 mL of StillVer Distillation Solution (2:1 Sulfuric Acid) into the flask. If high levels of chloride are present, add 5 mg silver sulfate for each mg/L chloride present.

FLUORIDE, continued

- d) Turn the heat control to setting 10, with the thermometer in place. The yellow pilot lamp shows when the heater is on.
- e) When the temperature reaches 180 °C (about one hour), turn the still off.
- f) Dilute the collected distillate to 100 mL, if necessary. Analyze the distillate by the above method.

Summary of Method

The SPADNS 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, thus bleaching the red color in an amount proportional to the fluoride concentration. Seawater and wastewater samples require distillation. See Optional Apparatus for Distillation Apparatus listing.

Pollution Prevention and Waste Management

SPADNS Reagent contains sodium arsenite. Final solutions will contain sodium arsenite (D004) in sufficient concentration to be regulated as hazardous waste for Federal RCRA. See *Section 3* for more information on disposal of these materials.

REQUIRED REAGENTS (Using Solution)

Description	Quantity Required		Cat. No.
	Per Test	Unit	
SPADNS Reagent for Fluoride	4 mL.....	500 mL.....	444-49
Water, deionized.....	10 mL	4 L.....	272-56

REQUIRED APPARATUS (Using Solution)

Pipet Filler safety bulb	1	each.....	14651-00
Pipet, volumetric, Class A, 10.00 mL.....	1	each.....	14515-38
Pipet, volumetric, Class A, 2.00 mL.....	1	each.....	14515-36
Sample Cell, 10-20-25 mL w/ cap	2	6/pkg.....	24019-06
Thermometer, -20 to 110°C, non-mercury	1	each.....	26357-02

REQUIRED REAGENTS (Using AccuVac Ampuls)

SPADNS Fluoride Reagent AccuVac Ampuls.....	2 ampuls.....	25/pkg.....	25060-25
Water, deionized.....	varies	4 L.....	272-56

FLUORIDE, continued

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL2each500-41H

OPTIONAL REAGENTS

Drinking Water Inorganics Standard

 for F^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} 500 mL28330-49

Fluoride Standard Solution, 0.2 mg/L F^- 500 mL405-02

Fluoride Standard Solution, 0.5 mg/L F^- 500 mL405-05

Fluoride Standard Solution, 0.8 mg/L F^- 500 mL405-08

Fluoride Standard Solution, 1.0 mg/L F^- 1000 mL291-53

Fluoride Standard Solution, 1.0 mg/L F^- 500 mL291-49

Fluoride Standard Solution, 1.2 mg/L F^- 500 mL405-12

Fluoride Standard Solution, 1.5 mg/L F^- 500 mL405-15

Fluoride Standard Solution, 2.0 mg/L F^- 500 mL405-20

Silver Sulfate, ACS 113 g334-14

Sodium Arsenite Solution 100 mL MDB1047-32

StillVer Distillation Solution 500 mL 446-49

OPTIONAL APPARATUS

AccuVac Snapper Kiteach24052-00

Cylinder, graduated, 100 mL.....each508-42

Cylinder, graduated, 250 mL.....each508-46

Distillation Heater and Support Apparatus Set, 115 V, 50/60 Hzeach22744-00

Distillation Heater and Support Apparatus Set, 230 V, 50/60 Hzeach22744-02

Distillation Apparatus General Purpose Accessorieseach22653-00

pH Meter, *sensio*[™]**I**, portable, with electrodeeach51700-10

Pipet, TenSette, 1.0 to 10.0 mLeach19700-10

Pipet Tips, for 19700-10 TenSette Pipet50/pkg21997-96

Stopper6/pkg1731-06

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.