



✓ Method 8029

SPADNS Method*

Reagent Solution or AccuVac® Ampuls

(0 to 2.00 mg/L F⁻)

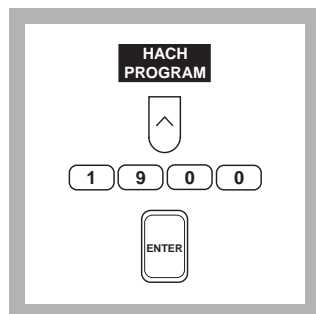
Scope and Application: For water, wastewater and seawater; USEPA accepted for reporting for drinking and wastewater analyses (distillation required; See “Distillation” on page 5).**

The estimated detection limit for program numbers 1900 and 1910 are 0.02 and 0.04 mg/L F⁻, respectively.

* Adapted from *Standard Methods for the Examination of Water and Wastewater*, 4500-F B & D

** Procedure is equivalent to USEPA method 340.1 for drinking water and wastewater.

Using SPADNS Reagent Solution



1. Press the soft key under **HACH PROGRAM**.

Select the stored program for fluoride (F⁻) by pressing **1900** with the numeric keys.

Press: **ENTER**

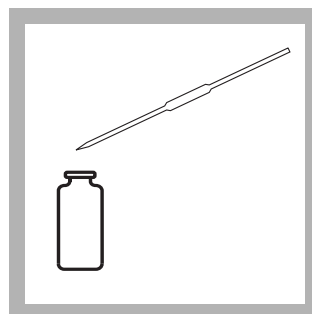
Note: If samples cannot be analyzed immediately, see *Sample Collection, Storage and Preservation* following these steps.

Note: The Flow Cell and Sipper Modules cannot be used for this procedure.



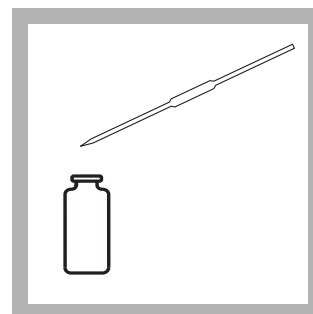
2. The display will show: **HACH PROGRAM: 1900 Fluoride**

The wavelength (λ), **580 nm**, is automatically selected.



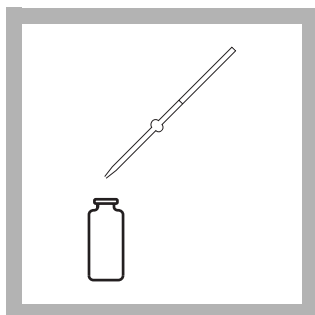
3. Pipet 10.0 mL of sample into a dry sample cell (the prepared sample).

Note: For proof of accuracy, use a 1.0 mg/L Fluoride Standard Solution (listed under **OPTIONAL REAGENTS AND STANDARDS**) in place of the sample.



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

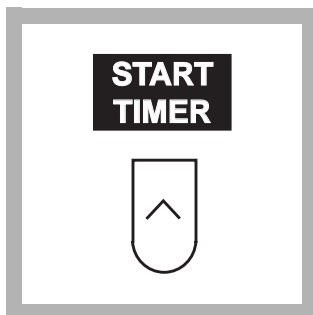
Note: The sample and deionized water should be at the same temperature (± 1 °C). Temperature adjustments may be made before or after reagent addition.



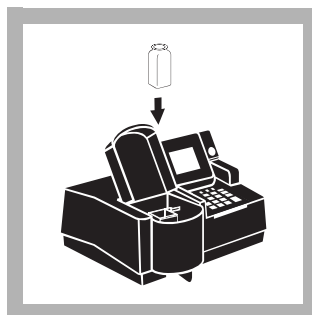
5. Use a pipet filler to pipet 2.0 mL of SPADNS Reagent into each cell. Swirl to mix.

Note: SPADNS Reagent is toxic and corrosive; use care while measuring.

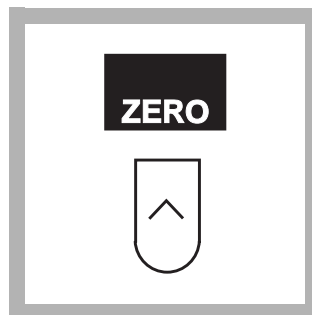
Note: The SPADNS Reagent must be measured accurately.



6. Press the soft key under **START TIMER**. A one minute reaction period will begin.



7. When the timer beeps, place the blank into the cell holder. Close the light shield.

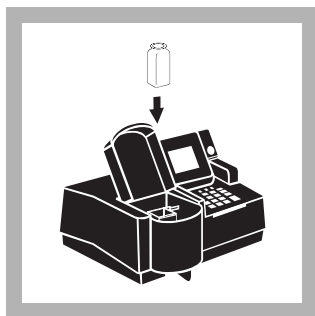


8. Press the soft key under **ZERO**.

The display will show:

0.00 mg/L F⁻

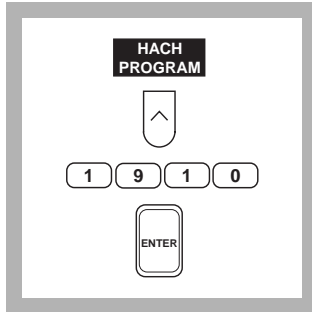
Note: For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.



9. Place the prepared sample into the cell holder. Close the light shield. Results in mg/L F⁻ (or chosen units) will be displayed.

Note: If the instrument displays **OVER!**, dilute a fresh sample with an equal volume of deionized water and repeat the test, using this solution in Step 3. Multiply the result by 2.

Using SPADNS AccuVac Ampuls

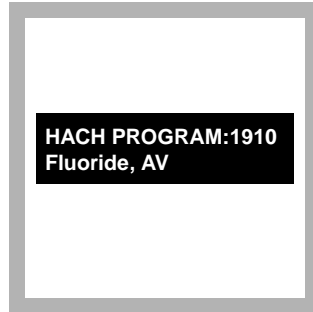


1. Press the soft key under **HACH PROGRAM**.

Select the stored program for fluoride AccuVac by pressing **1910** with the numeric keys.

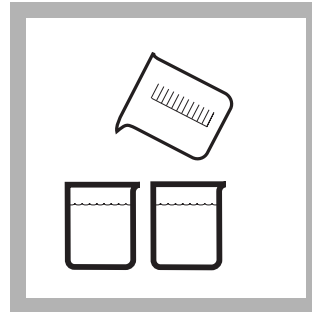
Press: **ENTER**

Note: If samples cannot be analyzed immediately, see *Sample Collection, Storage and Preservation* following these steps.

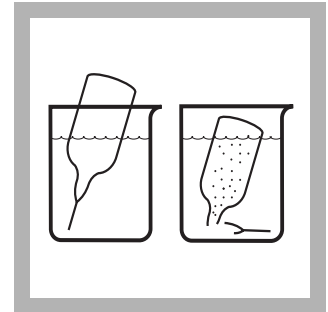


2. The display will show: **HACH PROGRAM: 1910 Fluoride, AV**

The wavelength (λ), **580 nm**, is automatically selected.



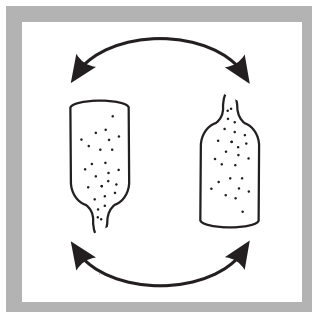
3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second beaker.



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) in the same manner.

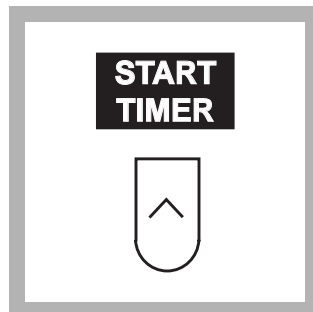
Note: Keep the tip immersed while the ampul fills completely.

Note: For proof of accuracy, use a 1.0 mg/L fluoride standard solution (listed under **OPTIONAL REAGENTS AND STANDARDS**) in place of the sample.



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

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



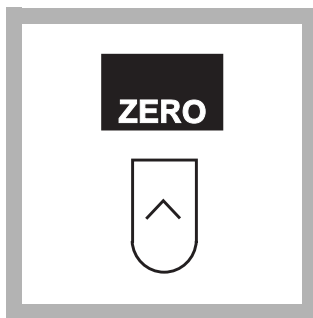
6. Press the soft key under **START TIMER**. A one-minute reaction period will begin.



7. Insert the AccuVac Ampul Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.



8. When the timer beeps, place the blank into the cell holder. Close the light shield.



9. Press the soft key under **ZERO**.

The display will show:

0.000 mg/L F⁻

Note: For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.

10. Place the AccuVac Ampul containing the sample into the instrument. Close the light shield. Results in mg/L F⁻ (or chosen units) will be displayed.

Note: If the instrument shows **OVER!** dilute a fresh sample with an equal volume of deionized water and repeat the test, using this solution in Step 3. Multiply the result by 2.

Interferences

This test is sensitive to small amounts of interference. Glassware must be very clean (acid rinse before each use). Repeating the test with the same glassware is recommended to ensure that results are accurate.

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
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 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 2 hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.
Chloride	At 7000 mg/L it causes a +0.1 mg/L F ⁻ error.
Chlorine	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.
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

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

1. Set up the distillation apparatus for general purpose distillation. Refer to the *Distillation Apparatus* manual for proper assembly. Use a 100-mL Erlenmeyer flask to collect the distillate.
2. Turn on the water and make certain a steady flow is maintained through the condenser.
3. Measure 100 mL of sample into the distillation flask using a 100-mL graduated cylinder. Add a magnetic stir bar and 5 glass beads.

Note: For proof of accuracy, use a 1.0-mg/L Fluoride Standard Solution (see *OPTIONAL REAGENTS AND STANDARDS*) in place of the sample.

4. Turn the stirrer power switch on. Turn the stir control to 5.
5. Using a 250-mL graduated cylinder, carefully add 150 mL of StillVer Distillation Solution into the flask.

Note: StillVer Distillation Solution is a 2:1 mixture of concentrated sulfuric acid and water. It is available already mixed from Hach.

Note: When distilling samples with high amounts of chloride, add 5 mg of Silver Sulfate to the sample for every mg/L of chloride in the sample.

6. With the thermometer in place, turn the heat control to 10. The yellow pilot lamp indicates that the heater is on.
7. When the temperature reaches 180 °C, or when 100 mL of distillate has been collected, turn the still off (requires about 1 hour).
8. Dilute the distillate to a volume of 100 mL, if necessary. The distillate may now be analyzed by the SPADNS or the fluoride ion-selective electrode method.

Sample Collection, Storage and Preservation

Samples may be stored in glass or plastic bottles for at least seven days when cooled to 4 °C (39 °F) or lower. Warm samples to room temperature before analysis.

Accuracy Check

Standard Solution Method

A variety of standard solutions covering the entire range of the test is 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.

To adjust the calibration curve using the reading obtained with a Fluoride Standard Solution, press the soft keys under **OPTIONS, MORE** then **STD: OFF**. Enter the actual value of the measured standards and press **ENTER**. See Section 1.5.5 *Adjusting the Standard Curve* for more information.

Method Performance

Precision

Standard: 1.00 mg/L F⁻

Program	95% Confidence Limits
1900	0.98–1.02 mg/L F ⁻
1910	0.97–1.03 mg/L F ⁻

For more information on determining precision data and method detection limits, refer to Section 1.5.

Estimated Detection Limit

Program	EDL
1900	0.02 mg/L F ⁻
1910	0.04 mg/L F ⁻

For more information on derivation and use of Hach's estimated detection limit, see Section 1.5.2. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see Section 1.5.1.

Sensitivity

Program Number 1900

Program	ΔAbs	ΔConcentration
0.010 Abs	0.010	-0.026 mg/L
1 mg/L	0.010	-0.023 mg/L
1.8 mg/L	0.010	-0.034 mg/L

Program Number 1910

Program	ΔAbs	ΔConcentration
0.010 Abs	0.010	-0.028 mg/L
1 mg/L	0.010	-0.025 mg/L
1.8 mg/L	0.010	-0.032 mg/L

See Section 1.5.3 *Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a fluoride calibration using the SPADNS Solution AccuVac method, prepare a 20-mg/L fluoride stock solution by pipetting 20.00 mL of a 100-mg/L Fluoride Standard Solution (Cat. No. 232-49) into a 100-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly.

Prepare calibration standard containing 0.20, 1.20, and 2.00 mg/L F⁻ as follows:

- a. Into three different 100-mL volumetric flasks, pipet 1.00, 6.00, and 10.00 mL of the 20 mg/L F⁻ stock solution using Class A glassware.
- b. Dilute to the mark with deionized water and mix thoroughly.
- c. Using the SPADNS Solution or AccuVac method and the calibration procedure described above, generate a calibration curve from the standards prepared above.

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. This method is accepted by the EPA for NPDES and NPDWR reporting purposes when the samples have been distilled. Seawater and wastewater samples require distillation. See *OPTIONAL REAGENTS AND STANDARDS* for Distillation Apparatus listing.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section 1.

Pollution Prevention and Waste Management

SPADNS Reagent contains sodium arsenite. Final solutions will contain arsenic (D004) in sufficient concentration to be regulated as a hazardous waste for Federal RCRA. See Section 1 for further information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS (Using Solution)

Description	Quantity Required		Unit	Cat. No.
	per test			
SPADNS Reagent Solution	4 mL	500 mL	444-49
Water, deionized	10 mL	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES (Using Solution)

DR/4000 1-Inch Cell Adapter	1	each	48190-00
Pipet Filler safety bulb	1	each	14651-00
Pipet, volumetric, Class A, 2.00-mL	1	each	14515-36
Pipet, volumetric, Class A, 10.00-mL	1	each	14515-38
Thermometer, -10 to 110 °C	1	each	1877-01

FLUORIDE, continued

REQUIRED REAGENTS AND STANDARDS (Using AccuVac Ampuls)

Description	Quantity Required per test	Unit	Cat. No.
SPADNS Fluoride Reagent AccuVac Ampuls	2 ampuls	25/pkg	25060-25
Water, deionized	varies	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES (Using AccuVac Ampuls)

Beaker, 50-mL	2	each	500-41
DR/4000 AccuVac Ampul Adapter	1	each	48187-00

OPTIONAL REAGENTS AND STANDARDS

Fluoride Standard Solution, 0.2 mg/L F ⁻	500 mL	405-02
Fluoride Standard Solution, 0.5 mg/L F ⁻	500 mL	405-05
Fluoride Standard Solution, 0.8 mg/L F ⁻	500 mL	405-08
Fluoride Standard Solution, 1.0 mg/L F ⁻	946 mL	291-16
Fluoride Standard Solution, 1.0 mg/L F ⁻	473 mL	291-11
Fluoride Standard Solution, 1.2 mg/L F ⁻	500 mL	405-12
Fluoride Standard Solution, 1.5 mg/L F ⁻	500 mL	405-15
Fluoride Standard Solution, 2.0 mg/L F ⁻	500 mL	405-20
Fluoride Standard Solution, 100 mg/L F ⁻	500 mL	232-49
Silver Sulfate, ACS	113 g	334-14
Sodium Arsenite Solution, 5.0 g/L	100 mL MDB	1047-32
StillVer Distillation Solution	500 mL	446-49

OPTIONAL EQUIPMENT AND SUPPLIES

AccuVac Snapper	each	24052-00
Cylinder, graduated, 100-mL	each	508-42
Cylinder, graduated, 250-mL	each	508-46
DR/4000 Carousel Module Kit	each	48070-02
Distillation Heater and Support Apparatus Set, 115 VAC, 50/60 Hz	each	22744-00
Distillation Heater and Support Apparatus Set, 230 VAC, 50/60 Hz	each	22744-02
Distillation Apparatus Set, General Purpose	each	22653-00
pH Meter, <i>sensio</i> TM 1, portable	each	51700-00
Pipet, volumetric, Class A, 1.00-mL	each	14515-35
Pipet, volumetric, Class A, 6.00-mL	each	14515-06
Pipet, volumetric, Class A, 10.00-mL	each	14515-38
Pipet, volumetric, Class A, 25.00-mL	each	14515-40



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