# Fluoride

DOC316.53.01041

### USEPA SPADNS Method<sup>1</sup>

### 0.02 to 2.00 mg/L F<sup>-</sup>

#### Method 8029

## Reagent Solution or AccuVac<sup>®</sup> Ampuls

**Scope and Application:** For water, wastewater and seawater; USEPA accepted for reporting for drinking and wastewater analyses (distillation required; see *Distillation* in this procedure).<sup>2</sup>

<sup>1</sup> Adapted from Standard Methods for the Examination of Water and Wastewater, 4500-F B & D.

<sup>2</sup> Procedure is equivalent to USEPA method 340.1 for drinking water and wastewater.

## Test preparation

# How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Instrument	Reagent	AccuVac Ampuls	
	Sample cell	Adapter	Adapter
DR 5000	2495402	A23618	A23618
DR 2800	2495402	—	LZV584 (C)
DR 2700	2495402	—	LZV584 (C)
DR/2500	2427606	—	—
DR/2400	2427606	_	—

#### Table 1 Instrument-specific information

#### Before starting the test:

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

SPADNS Reagent is toxic and corrosive. Use care while handling the reagent.

SPADNS Reagent contains sodium arsenite. Final solutions will contain arsenic (D004) in sufficient concentration to be regulated as a hazardous waste for Federal RCRA. Refer to the MSDS for disposal instructions.

For best results, measure the volume of SPADNS Reagent as accurately as possible.

Do not use the Pour-Thru Cell with this test.

#### Collect the following items:

Description	Quantity
Solution Test:	
SPADNS Reagent Solution	4 mL
Deionized Water	10 mL
Pipet, volumetric, 2-mL	1

#### Collect the following items: (continued)

Description	Quantity
Pipet, volumetric, 10-mL	1
Pipet Filler Bulb	1
Sample cells (Instrument-specific information)	2
Thermometer, -10 to 110 °C	1
AccuVac Test:	
SPADNS Fluoride Reagent AccuVac <sup>®</sup> Ampuls	2
Deionized Water	40 mL
Beaker, 50-mL	1
Stopper	2

See Consumables and replacement items for reorder information.

#### SPADNS reagent solution method



**1.** Select the test. Insert an adapter if required (*Instrument-specific information*).

Refer to the user manual for orientation.



**5.** Start the instrument timer.

A one-minute reaction period will begin.



**2. Prepared Sample**: Pipet 10.0 mL of sample into a dry sample cell.



**3. Blank Preparation**: Pipet 10.0 mL of deionized water into a second dry sample cell.



**4.** Carefully pipet 2.0 mL of SPADNS Reagent into each cell. Swirl to mix.



**6.** When the timer expires, insert the blank into the cell holder.



 ZERO the instrument.
The display will show: 0.00 mg/L F<sup>-</sup>



 Insert the prepared sample into the cell holder.
READ the result in

mg/L F⁻.

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# SPADNS AccuVac® Ampuls



**1.** Select the test. Insert an adapter if required (*Instrument-specific information*).

Refer to the user manual for orientation.



**5.** Start the instrument timer.

A one-minute reaction period will begin.



2. Prepared Sample: Collect at least 40 mL of sample in a 50-mL beaker.

Fill one SPADNS Fluoride Reagent AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



**3. Blank Preparation:** Pour at least 40 mL of deionized water into a second beaker.

Fill a second Ampul with deionized water. Keep the tip immersed while the Ampul fills completely.



**4.** Close with stopper and Quickly invert both Ampuls several times to mix.

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**6.** When the timer expires, wipe the blank and insert it into the cell holder.

ZERO the instrument.

The display will show:

0.00 mg/L F-



**7.** Insert the Ampul that contains the prepared sample into the cell holder.

**READ** the results in mg/L F<sup>-</sup>.

#### Interferences

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

Interfering substance	Interference level		
Alkalinity (as CaCO <sub>3</sub> )	At 5000 mg/L it causes a - 0.1 mg/L F <sup>_</sup> error.		
Aluminum	At 0.1 mg/L it causes a - 0.1 mg/L F <sup>-</sup> 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 causes a +0.1 mg/L F <sup>-</sup> 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 <sup>1</sup> 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 <sup>-</sup> error.		
Phosphate, ortho	At 16 mg/L it causes a +0.1 mg/L F <sup>-</sup> error.		
Sodium Hexametaphosphate	At 1.0 mg/L it causes a +0.1 mg/L F <sup>-</sup> error.		
Sulfate	At 200 mg/L it causes a +0.1 mg/L F <sup>-</sup> error.		

<sup>1</sup> See Optional reagents and apparatus.

## 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 125-mL Erlenmeyer flask to collect the distillate.
- 2. Turn on the water and maintain a steady flow 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.
- 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<sup>®</sup> Distillation Solution into the flask. (StillVer Distillation Solution is a 2:1 mixture of concentrated sulfuric acid and water.)

**Note:** When distilling samples with high amounts of chloride, add 5 mg of Silver Sulfate<sup>\*</sup> 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 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).

<sup>\*</sup> See Optional reagents and apparatus.

**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, preservation and storage

- 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

Note: Refer to the instrument user manual for specific software navigation instructions.

A variety of standard solutions covering the entire range of the test is available. Use these instead 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.

**1.** To adjust the calibration curve using the reading obtained with the 1.00-mg/L Standard Solution, navigate to Standard Adjust in the software.

Instrument	Navigate to:
DR 5000	OPTIONS>MORE>STANDARD ADJUST
DR 2800	OPTIONS>MORE>STANDARD ADJUST
DR 2700	OPTIONS>MORE>STANDARD ADJUST
DR/2500	OPTIONS>STANDARD ADJUST
DR/2400	OPTIONS>STANDARD ADJUST

**2.** Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

# Method performance

Program	Instrument	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
190	DR 5000	1.00 mg/L F-	0.97–1.03 mg/L F <sup>_</sup>	0.024 mg/L F <sup>_</sup> at 1 mg/L
	DR 2800			
	DR 2700			
	DR/2500	1.00 mg/L F-	0.95–1.05 mg/L F <sup>_</sup>	0.03 mg/L F⁻ at 0 ppm
	DR/2400	*		0.03 mg/L F⁻ at 1 ppm 0.04 mg/L F⁻ at 2 ppm
195	DR 5000	1.00 mg/L F-	0.92–1.08 mg/L F⁻	0.03 mg/L F <sup>-</sup> at 1 mg/L
	DR 2800			
	DR 2700			
	DR/2500	1.00 mg/L F-	0.88–1.12 mg/L F⁻	0.02 mg/L F <sup>_</sup> at 0 ppm
	DR/2400			0.03 mg/L F <sup>_</sup> at 1 ppm 0.04 mg/L F <sup>_</sup> at 2 ppm

# 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. Test results are measured at 580 nm.

## **Consumables and replacement items**

#### **Required reagents**

Description	Quantity/Test	Unit	Catalog number
SPADNS Reagent Solution	4 mL	500 mL	44449
OR			
SPADNS Fluoride Reagent AccuVac® Ampuls	2	25/pkg	2506025
Water, deionized	10–40 mL	4 L	27256

#### **Required apparatus (solution)**

Description	Quantity/Test	Unit	Catalog number
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, -10 to 110 °C	1	each	187701

#### Required apparatus (AccuVac)

Description	Quantity/Test	Unit	Catalog number
Beaker, 50-mL	1	each	50041H

#### **Recommended standards**

Description	Unit	Catalog number
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 <sup>-</sup>	500 mL	40508
Fluoride Standard Solution, 1.0-mg/L F-	1000 mL	29153
Fluoride Standard Solution, 1.0-mg/L F <sup>_</sup>	500 mL	29149
Fluoride Standard Solution, 1.2-mg/L F <sup>-</sup>	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
Standard, Drinking Water, Mixed Parameter, Inorganic for F <sup>−</sup> , NO <sub>3</sub> , PO <sub>4</sub> , SO <sub>4</sub>	500 mL	2833049

#### Distillation reagents and apparatus

Description	Quantity/Test	Unit	Catalog number
Cylinder, graduated, 100-mL	1	each	50842
Cylinder, graduated, 250-mL	1	each	50846
Distillation Heater and Support Apparatus Set,115 VAC, 50/60 Hz	1	each	2274400
OR			
Distillation Heater and Support Apparatus Set, 230 VAC, 50/60 Hz	1	each	2274402
AND			
Distillation Apparatus Set, General Purpose	1	each	2265300
Flask, Erlenmeyer, 125-mL	1	each	2089743
Glass Beads	1	100/pkg	259600
StillVer <sup>®</sup> Distillation Solution	varies	500 mL	44649
Stir Bar, magnetic	1	each	1076416

#### Optional reagents and apparatus

Description	Unit	Catalog number
Silver Sulfate	113 g	33414
Sodium Arsenite Solution, 5.0 g/L	100 mL	104732
AccuVac Snapper,	each	2405200
Wipes, disposable	280/pkg	2097000



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