

## USEPA SPADNS or SPADNS2 Method<sup>1</sup>

## Method 8029 (SPADNS) and Method 10225 (SPADNS2)

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

Reagent Solution

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

#### Before starting

The sample and deionized water must be at the same temperature ( $\pm 1$  °C). Temperature adjustments can be made before or after the reagent addition.

Make sure that the sample cells are clean and dry before the test.

Measure the volume of the reagent accurately. Use a volumetric or high precision pipet if possible.

The reagent that is used in this test is corrosive and toxic. Use protection for eyes and skin and be prepared to flush any spills with running water.

Use SPADNS or SPADNS2 Fluoride Reagent for this procedure. SPADNS Fluoride Reagent contains sodium arsenite to prevent chlorine interference. SPADNS2 Fluoride Reagent contains a non-toxic reducing agent to prevent chlorine interference. Both reagents are accepted for regulatory reporting. The stored instrument calibrations for the two reagents are equivalent. The calibration procedure steps apply to either reagent.

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.

Always do tests in sample cells. Do not put the instrument in the sample or pour the sample into the cell holder.

Make sure that the sample cells are clean and there are no scratches where the light passes through them.

Rinse the sample cell and cap with the sample three times before the sample cell is filled.

Make sure that there are no fingerprints or liquid on the external surface of the sample cells. Wipe with a lint-free cloth before measurement.

Cold waters can cause condensation on the sample cell or bubbles in the sample cell during color development. Examine the sample cell for condensation or bubbles. Remove condensation with a lint-free cloth. Invert the sample cell to remove bubbles.

Install the instrument cap over the cell holder before ZERO or READ is pushed.

After the test, immediately empty and rinse the sample cell. Rinse the sample cell and cap three times with deionized water.

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.

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

Description	Quantity
SPADNS or SPADNS2 Fluoride Reagent AccuVac Ampul	4 mL
Deionized water	10 mL

## Items to collect (continued)

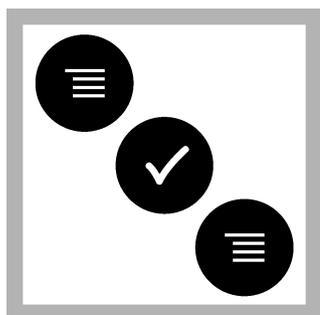
Description	Quantity
Pipet, volumetric, 2-mL	1
Pipet filler bulb	1
Pipet, volumetric, 10-mL	1
Thermometer, -10 to 110 °C	1
Sample cells, 25-mm (10 mL)	2

Refer to [Consumables and replacement items](#) on page 5 for order information.

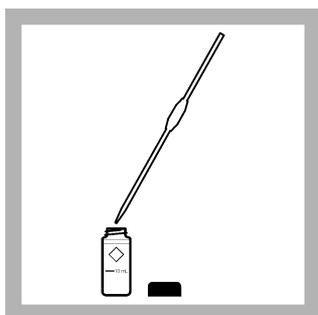
## Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 4 °C (39 °F) for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

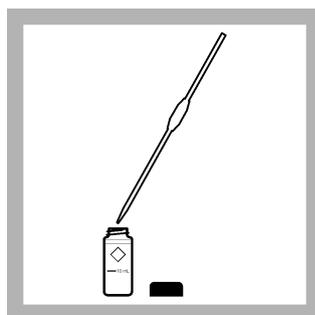
## Reagent solution procedure



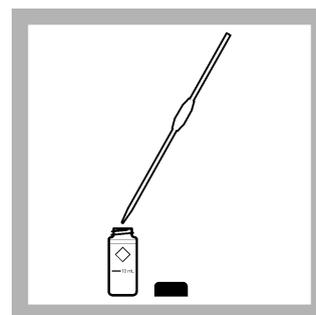
1. Set the instrument to channel 1. Refer to the instrument documentation.



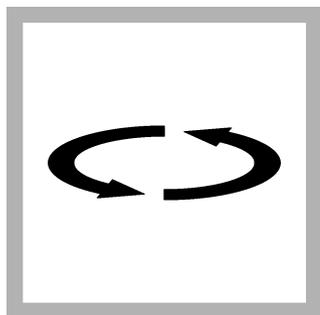
2. **Prepare the blank:** Use a pipet to add 10.0 mL of deionized water to a dry sample cell.



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



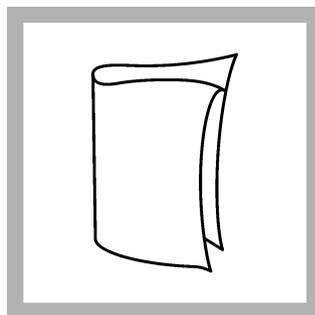
4. Use a pipet to add 2.0 mL of SPADNS or SPADNS2 Reagent Solution to each sample cell.



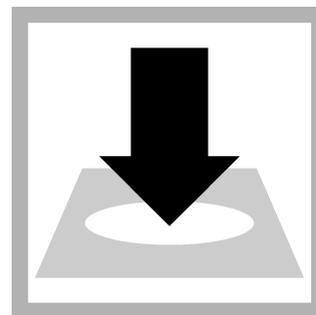
5. Swirl to mix.



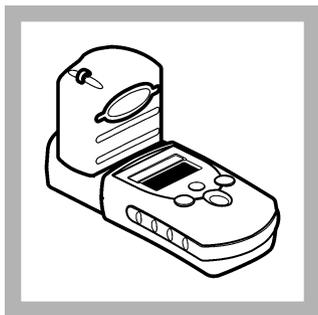
6. Set and start a timer for 1 minute. A 1-minute reaction time starts.



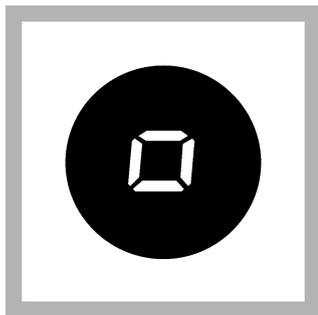
7. When the timer expires, clean the blank sample cell.



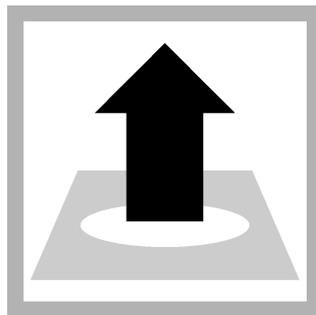
8. Insert the blank into the cell holder. Point the diamond mark on the sample cell toward the keypad.



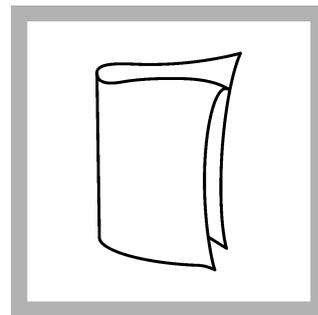
9. Install the instrument cap over the cell holder.



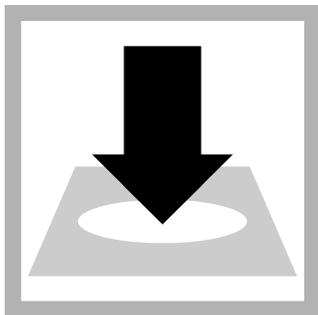
10. Push **ZERO**. The display shows "0.00".



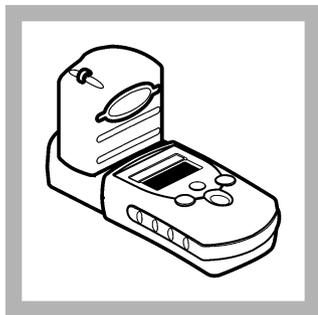
11. Remove the sample cell from the cell holder.



12. Clean the prepared sample cell.



13. Insert the prepared sample into the cell holder. Point the diamond mark on the sample cell toward the keypad.



14. Install the instrument cap over the cell holder.



15. Push **READ**. Results show in mg/L fluoride (F<sup>-</sup>).

## 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 <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 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 <sup>-</sup> error.
Chlorine	SPADNS Reagent contains enough arsenite to remove up to 5 mg/L chlorine. For higher chlorine levels, add 1 drop of Sodium Arsenite Solution, 5.0 g/L, to 25 mL of sample to remove each additional 2 mg/L of Chlorine. SPADNS2 Reagent contains sufficient non-toxic reductant to remove interference of up to 5 mg/L chlorine. For higher chlorine levels: <ol style="list-style-type: none"> <li>1. Dilute the sample with deionized water by a factor that will decrease the chlorine concentration to less than 5 mg/L.</li> <li>2. Use the test procedure to measure the fluoride concentration.</li> <li>3. Multiply the result by the dilution factor to get mg/L fluoride.</li> </ol>
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.

Interfering substance	Interference level
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.

## 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.

## Pollution prevention and waste management

SPADNS Fluoride Reagent (not SPADNS2) reacted samples contain sodium arsenite and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

## Accuracy check

### Standard solution method

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

Items to collect:

- 1.00 mg/L Fluoride Standard Solution

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 calibration 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 Pocket Colorimeter II during ideal test conditions. Users can get different results under different test conditions.

Precision (95% confidence interval)
1.00 ± 0.06 mg/L F <sup>-</sup>

## 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.

## Consumables and replacement items

### Required reagents

Description	Quantity/test	Unit	Item no.
SPADNS 2 Reagent Solution	4 mL	500 mL	2947549
SPADNS Reagent Solution	4 mL	500 mL	44449
Water, deionized	varies	4 L	27256

### Required apparatus

Description	Quantity/test	Unit	Item no.
Sample cells, 10-mL round, 25 mm x 60 mm	2	6/pkg	2427606
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 °C to 110 °C	1	each	187701

### Recommended standards

Description	Unit	Item no.
Fluoride Standard Solution, 0.2-mg/L F <sup>-</sup>	500 mL	40502
Fluoride Standard Solution, 0.5-mg/L F <sup>-</sup>	500 mL	40505
Fluoride Standard Solution, 0.8-mg/L F <sup>-</sup>	500 mL	40508
Fluoride Standard Solution, 1.0-mg/L F <sup>-</sup>	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 <sup>-</sup>	500 mL	40515
Fluoride Standard Solution, 2.0-mg/L F <sup>-</sup>	500 mL	40520
Drinking Water Standard, Mixed Parameter, Inorganic for F <sup>-</sup> , NO <sub>3</sub> -N, PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	500 mL	2833049

## Distillation reagents and apparatus

Description	Unit	Item no.
Graduated cylinder, 100-mL	each	50842
Graduated cylinder, 250-mL	each	50846
Distillation heater and support for apparatus set, 115 VAC option	each	2274400
OR		
Distillation heater and support for apparatus set, 230 VAC option	each	2274402
AND		
Distillation apparatus set, general purpose	each	2265300
Flask, Erlenmeyer, 125-mL	each	2089743
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
Sodium Arsenite, 5-g/L	100 mL	104732
SpecCheck Secondary Standards Kit, Fluoride	each	2712500
AccuVac <sup>®</sup> Ampul Snapper	each	2405200
Wipes, disposable	280/pkg	2097000



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