

Fluoride in Pure Water (0.1 to 1.0 mg/L) by Direct Measurement

Key Words

- Fluoride
- Pure Water
- Fluoride Ion Selective Electrode (ISE)

Introduction

In the following method, fluoride concentrations at low levels in pure water are determined by direct measurement with the Thermo Scientific Orion combination fluoride electrode, Thermo Scientific Orion 4-Star Plus meter and Thermo Scientific Orion fluoride standards pre-mixed with TISAB II. The calibration is linear from 0.1 to 10 mg/L fluoride.

Recommended Equipment

	Cat. No.
1. 4-Star Plus benchtop pH/ISE meter	1115000
2. Fluoride combination electrode	9609BNWP
3. Stirrer probe (or magnetic stir plate and bar)	096019
4. Swing arm electrode stand	090043
5. ATC probe (optional)	927005MD
6. 50 and 100 mL beakers	
7. 50 mL graduated cylinders	

Required Solutions

	Cat. No.
1. 1 mg/L fluoride standard with TISAB II	040906
2. 2 mg/L fluoride standard with TISAB II	040907
3. 10 mg/L fluoride standard with TISAB II	040908
4. Optimum Results™ A electrode filling solution	900061
5. TISAB II solution	940909
6. Deionized water	

Calibration Standard Preparation

1. Using a graduated cylinder, add 30 mL of the 1 mg/L fluoride standard pre-mixed with TISAB II (Cat. No. 040906) into a clean 50 mL beaker.
2. Using a graduated cylinder, add 30 mL of the 2 mg/L fluoride standard pre-mixed with TISAB II (Cat. No. 040907) into a clean 50 mL beaker.
3. Using a graduated cylinder, add 30 mL of the pre-mixed 10 mg/L fluoride standard pre-mixed with TISAB II (Cat. No. 040908) into a clean 50 mL beaker.
4. Using a graduated cylinder, prepare a 0.5 mg/L fluoride standard by adding 20.0 mL of the 1 mg/L fluoride standard (Cat. No. 040906), 10.0 mL of TISAB II (Cat. No. 940909) and 10.0 mL of deionized water into a clean 100 mL beaker. Mix the solution well. This solution can be used to check the calibration.

Sample Preparation

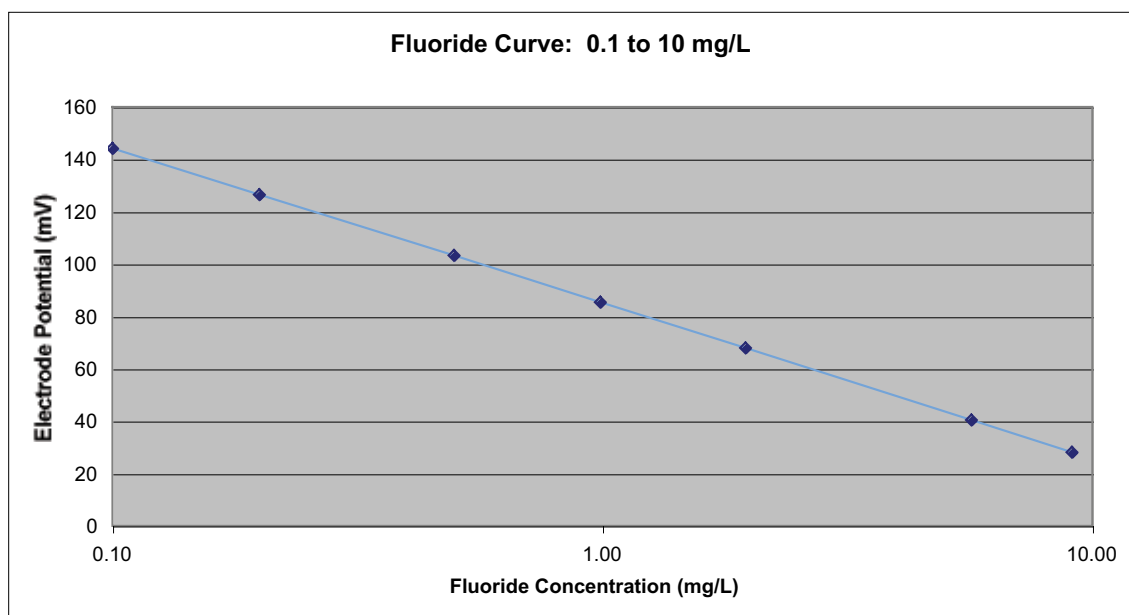
1. Using a graduated cylinder, add 15.0 mL of sample into a clean 50 mL beaker. Add 15.0 mL of TISAB II (Cat. No. 940909) to the same beaker for a total volume of 30 mL. If a magnetic stir plate will be used, add a clean, dry stir bar to the beaker.
2. Repeat step 1 for additional samples.

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Results

Fluoride response was tested between 0.1 and 10 mg/L. Response is linear over the entire range. Therefore, calibration at 1, 2 and 10 mg/L will give accurate results down to 0.1 mg/L.

Actual Fluoride Concentration (mg/L)	Measurement Results (mg/L)	Measurement Results (mV)	Response Time (minutes)	% R	RSD or % D
1	1.02	103.5	1.0	102%	1.3%
1	1.04	103.0	1.5	104%	
1	1.04	103.0	1.5	104%	
1	1.05	102.5	1.5	105%	
0.5	0.507	121.2	1.5	101%	3.2%
0.5	0.523	120.4	2.0	105%	
0.2	0.198	143.7	2.0	99%	4.5%
0.2	0.207	142.8	2.0	104%	
0.1	0.0895	160.6	2.0	90%	3.0%
0.1	0.0917	160.1	1.5	92%	
0.1	0.0961	159.2	1.5	96%	
0.1	0.0947	159.5	3.0	95%	



Electrode Storage

The filling solution inside the fluoride electrode should not be allowed to evaporate, as crystallization will result. Between measurements, rinse the fluoride electrode with deionized water and blot it dry with a lint-free tissue.

For brief storage periods between sample measurements, store the electrode in a 4 M potassium chloride solution with fluoride. The fluoride concentration of the storage solution should be close to the least concentrated fluoride calibration standard. Do not add TISAB II to the storage solution.

For storage periods longer than one week, drain the electrode, flush the chamber with distilled water and store the electrode dry with the protective shipping cap covering the sensing element.

Equipment Setup

Electrode Setup – Fluoride Electrode

1. Remove the protective shipping cap that covers the electrode tip.
2. Attach the flip-spout cap to the Optimum Results A filling solution bottle and lift the spout to a vertical position. Insert the spout into the electrode fill hole, add a small amount of filling solution to the chamber, tip the electrode upsidedown to wet the O-ring and return the electrode to its original position.
3. Holding the electrode by the body with one hand, use the thumb to push down on the electrode cap and allow a few drops of filling solution to drain wetting the inner cone. Release the electrode cap and allow the outer sleeve to return to its original position. If the outer sleeve does not return to its original position, check if the O-ring is moist and repeat steps 2 and 3 until the outer sleeve returns to its original position.
4. Add filling solution to the electrode until the amount of filling solution within the electrode body is level with the bottom edge of the electrode fill hole.

Meter Setup – 4-Star Plus Benchtop pH/ISE Meter

For initial meter setup, follow the steps in the quick start guide that is included with the meter. The quick start guide also contains a layout of the meter keypad for reference. The words in all capital letters, such as POWER, indicate a key on the meter and words in quotations, such as “UnIt”, indicate a display on the meter screen.

1. Connect the electrode and ATC probe (if used) to the meter.
2. Connect the stirrer probe to the meter. If a magnetic stir plate will be used, clean and dry several stir bars.
3. Press the POWER key to turn on the meter.
4. The arrow icon on the left of the screen indicates the active line. If the top line is not active, press the LINE SELECT key to change the selected line to the top line. Press the UP or DOWN ARROW key to change the measurement mode on the top line to ISE.
5. Press the SETUP key.
6. Press the UP or DOWN ARROW key until “rEAd” is displayed on the top line.
7. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “rYPE”, which is for the read type. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “COnt” for the continuous read type. Press the LINE SELECT key to accept the setting.
8. Press the UP or DOWN ARROW key until “LOG” is displayed on the top line.
9. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “AUtO”, which is for enabling or disabling the datalog. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “On” to enable the datalog. Press the LINE SELECT key to accept the setting.
10. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “dEL”, which is for the automatic deletion of the datalog when it becomes full. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “nO” to allow the meter to automatically delete the datalog when it is full. Press the LINE SELECT key to accept the setting.
11. Press the UP or DOWN ARROW key until “ISE” is displayed on the top line.
12. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “rES”, which is for ISE resolution and the number of significant digits that will be displayed on the meter. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “3” for “rES”. Press the LINE SELECT key to accept the setting.
13. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “nLIn”, which is an abbreviation for non-linear blank correction. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “OFF” for “nLIn”. Press the LINE SELECT key to accept setting.
14. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “rAng”, which is an abbreviation for the measurement range type. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “HIgH” for “rAng”. Press the LINE SELECT key to accept setting.
15. Press the LINE SELECT key to select the middle line. Press the UP or DOWN ARROW key to select “UnIt”. Press the LINE SELECT key to select the bottom line. Press the UP or DOWN ARROW key to select “mgL” for “UnIt”. Press the LINE SELECT key to accept setting.
16. Press the MEASURE key to return to the measurement mode.
17. If all steps were followed correctly, the meter display will show three digits in the top line and “ISE: mg/L” to the right of the top line. If an ATC probe is used, the temperature will be displayed in the top, left of the screen. The meter and electrode are now ready for calibration.

Calibration and Analysis

1. Allow all standards and samples to reach room temperature for precise measurements, since fluoride measurements are temperature sensitive.
2. Prepare the 1 mg/L, 2 mg/L and 10 mg/L fluoride standards as described in the Calibration Standard Preparation section. Due to linear response of the fluoride electrode, results are accurate to 0.1 mg/L. See the fluoride curve in the Results section.
3. Place the electrode, stirrer probe or stir bar and ATC probe (if used) into the beaker with the 1 mg/L standard so the electrode tip is fully immersed in the solution. The stirrer probe should be positioned slightly below the tip of the electrode. Press the STIR key to turn on the stirrer probe or place the beaker on the magnetic stir plate and set it to a moderate stir rate.
4. In the measurement mode, press the LINE SELECT key to change the selected line (indicated by the arrow icon on the left of the screen) to the top line. Press the UP or DOWN ARROW key to change the measurement mode of the top line to mV. Allow the electrode to stabilize and wait until the measurement changes by no more than 0.5 mV per minute.
5. Press the UP or DOWN ARROW key to change the measurement mode of the top line to ISE: mg/L.
6. Press the CALIBRATE key.
7. Wait for a stable reading, usually in 1 to 2 minutes. Enter the standard value of "1.00" using the DIGIT key and UP and DOWN ARROW keys. Press the DIGIT key until the first digit to be changed is flashing, press the UP and DOWN ARROW keys to change the value of the flashing digit and continue to change the digits until the meter displays the correct value of the standard. Once the value is set, press the DIGIT key until the decimal point is in the correct location.
8. Press the CALIBRATE key to accept the 1.0 mg/L standard and press the STIR key to turn off the stirrer probe or remove the beaker from the magnetic stir plate.
9. Rinse the electrode, ATC probe (if used) and stirrer probe or stir bar thoroughly with deionized water and blot dry with a lint-free tissue. Gently remove excess solution from the outer sleeve of the electrode by dabbing it with a clean tissue. Do not wipe or rub the sensing element of the electrode.
10. Place the electrode, ATC probe (if used) and stirrer probe or clean, dry stir bar into the beaker with the 2.0 mg/L standard so the electrode tip is fully immersed in the solution. The stirrer probe should be positioned slightly below the tip of the electrode. Press the STIR key to turn on the stirrer probe or place the beaker on the magnetic stir plate and set it to a moderate stir rate.
11. Wait for a stable reading. Enter the standard value of "2.00" using the DIGIT key and UP and DOWN ARROW keys.
12. Press the CALIBRATE key to accept the 2.0 mg/L standard and press the STIR key to turn off the stirrer probe or remove the beaker from the magnetic stir plate.
13. Rinse the electrode, ATC probe (if used) and stirrer probe or stir bar thoroughly with deionized water and blot dry with a lint-free tissue. Gently remove excess solution from the outer sleeve of the electrode by dabbing it with a clean tissue. Do not wipe or rub the sensing element of the electrode.
14. Place the electrode, ATC probe (if used) and stirrer probe or clean, dry stir bar into the beaker with the 10.0 mg/L standard so the electrode tip is fully immersed in the solution. The stirrer probe should be positioned slightly below the tip of the electrode. Press the STIR key to turn on the stirrer probe or place the beaker on the magnetic stir plate and set it to a moderate stir rate.
15. Wait for a stable reading. Enter the standard value of "10.0" using the DIGIT key and UP and DOWN ARROW keys.
16. Press the MEASURE key to accept the 10.0 mg/L standard and return to the measurement mode. The meter will display the electrode slope value for about 4 seconds. The slope should be 54 to 60 mV/decade. Press the STIR key to turn off the stirrer probe or remove the beaker from the magnetic stir plate.
17. Rinse the electrode, ATC probe (if used) and stirrer probe or stir bar thoroughly with deionized water and blot dry with a lint-free tissue. Gently remove excess solution from the outer sleeve of the electrode by dabbing it with a clean tissue. Do not wipe or rub the sensing element of the electrode.
18. Prepare a sample as described in the Sample Preparation section.
19. Place the electrode, ATC probe (if used) and stirrer probe or clean, dry stir bar into a prepared sample with the electrode tip fully immersed in the solution. Press the STIR key to turn on the stirrer probe or place the beaker on the magnetic stir plate and set it to a moderate stir rate. The ISE:mg/L icon will flash as the measurement is being made and the ISE:mg/L icon will become solid when a stable measurement is achieved. A stable measurement is usually achieved in 2 to 3 minutes.
20. Record the stable measurement and press the MEASURE key to print and log the measurement. Press the STIR key to turn off the stirrer probe or remove the beaker from the magnetic stirrer.
21. Repeat steps 17 through 20 for additional samples. When all samples have been measured, rinse the electrode with deionized water and store the electrode according to the Electrode Storage section.

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