



Parameter & Sample Type

Fluoride in Pure Water (0.1 – 1.0 mg/L) by known addition

Introduction

Fluoride at low levels in pure water is determined by method of known addition measurement with the Orion 9609BN combination fluoride electrode on an Orion dual channel meter with incremental techniques capability. Additions (1.0 and 10.0 mL) of 100 mg/L Orion fluoride standard are spiked into the sample by the user and the sample concentration is automatically calculated by the meter. No calibration is necessary.

References

1. Method 4500-F⁻ C, Ion Selective Electrode Method, known-additions method option. Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998. APHA, AWWA, & WEF, Washington, D.C.
www.standardmethods.org

Result Statistics

See the second page

Recommended Equipment

Orion dual channel meter w/ incremental techniques (Orion 2115000 or Orion 920A) ; Fluoride electrode (Orion 9609BN); magnetic stirrer for 920A meter or Orion 096019 paddle stirrer for Star meter; automatic pipet, e.g., Thermo Scientific no. 4600410 (1-10mL) or 4600400 (0.5-5mL) or glass pipets; 50 mL graduated cylinder; 250 mL volumetric flask.

Required Solutions

100 mg/L Fluoride standard (940907); TISAB II (940909); deionized water (DI).

Solutions Preparation

Recommended: each day prepare a mid-range check standard at 0.4 mg/L by pipeting 1.0 mL of 100 mg/L fluoride standard into a 250 mL volumetric flask and diluting to the mark with DI.

Meter Setup

Connect the electrode to channel 1 or 2, and set up for stirring (magnetic or paddle stirrer). Follow meter manual setup for Fluoride by ISE measurement. Select the channel (1 or 2) and set the electrode ID as fluoride (F⁻). Select resolution of 3 digits and concentration units of mg/L (ppm) on Orion 2115000.

Electrode Setup

See the electrode manual for (assembling and) preparation of the electrode.

Electrode Performance Check

Check slope at least daily according to the electrode manual. Drift may be checked by comparing a 1 minute to a 2 minute reading. Results should agree with desired criteria. See troubleshooting section of manual if slope or drift problems.

Electrode Storage, Soaking, and Rinsing

See electrode manual for storage 1) between measurements, 2) overnight, and 3) for long periods of time. Between measurements, rinse the electrode with DI water.

Sample Preservation

Collect fluoride samples in plastic. No sample preservation is required. A collected sample is valid for 28 days. Refer to reference(s) and/or EPA 40 CFR Part 136.3 for details.

Sample Preparation

For precise measurements, allow all the standards and the samples to reach the same temperature before analysis. Measure 50.0 mL sample into a 150-mL beaker. Add 50.0 mL TISAB II to the beaker for a total volume of 100 mL. If using magnetic stirrer, add a clean dry stir bar. For a smaller volume procedure, see page 2.

Calibration

The double known addition measurement is used instead of a direct calibration. Sample concentration and electrode slope are determined automatically by the meter via two additions of a known standard to the sample. Check accuracy by testing the 0.4 mg/L check standard prepared daily. Results should be close to 0.4 mg/L, within the user-determined tolerance.

Analysis

Rinse electrode and stirrer (if using Star meter) with DI water and place in the prepared sample. Follow the meter instructions for double known addition measurement procedure. Enter the following information when prompted:

Sample volume	50 mL
Total volume	100 mL
Std concentration	100 mg/L
1 st std vol added	1.0 mL
2 nd std vol added	10.0 mL

Briefly, the meter will determine initial mV value of the sample plus ISA, then will prompt for the 1st known addition. The user will pipet 1.0 mL of 100 mg/L standard into the same beaker. The meter will determine this mV value and prompt for the 2nd known addition. The user will pipet 10.0 mL of 100 mg/L standard into the same beaker. The meter will determine this mV value, then calculate slope (in mV) and sample concentration (in mg/L). A slope of 54-60 mV indicates a good analysis.



Quality Control (QC)

Recommended QC procedures include: calibration check samples, initial demonstration of laboratory capability and method detection limit determination, laboratory control samples (LCS), method blanks, matrix spikes (MS), sample duplicates, and independent reference materials. See references above for details.

Testing Results:

Results of Testing by DKA (double known addition) 50 mL sample volume			
Fluoride in Pure Water	Result (mg/L)	Recovery (%R)	Duplicate Precision
1.0 mg/L	1.02	102%	1.0%
1.0 mg/L	1.01	101%	
0.5 mg/L	0.506	101%	0.4%
0.5 mg/L	0.508	102%	
0.2 mg/L	0.206	103%	2.4%
0.2 mg/L	0.211	106%	
0.1 mg/L	0.108	108%	0.9%
0.1 mg/L	0.107	107%	

Instructions for Smaller Volume Sample Preparation

Preparation: For precise measurements, allow all the standards and the samples to reach the same temperature before analysis. Measure 25.0 mL of sample into a 100-mL beaker. Add 25.0 mL of TISAB II to the beaker for a total volume of 50.0 mL. If using magnetic stirrer, add a clean dry stir bar.

Analysis: Rinse electrode and stirrer (if using Star meter) with DI water and place in the prepared sample. Follow the meter instructions for double known addition measurement procedure. Enter the following information when prompted:

Sample volume	25 mL
Total volume	50 mL
Std concentration	100 mg/L
1 st std vol added	0.5 mL
2 nd std vol added	5.0 mL