



Fluoride by ISE and Combined Flow Injection Analysis (FIA) and Segmented Flow Analysis (SFA)

(Cartridge Part #A002677)

1.0 Scope and Application

- 1.1 This method is used for the determination of fluoride in drinking water, surface water, and domestic and industrial wastes using an ion-selective electrode (ISE) (Reference 15.2).
- 1.2 The Method Detection Limit (MDL) of this method is 0.005 mg/L fluoride. The applicable range of the method is 0.20–8.0 mg/L fluoride. The range may be extended to analyze higher concentrations by sample dilution.

2.0 Summary of Method

- 2.1 Fluoride is determined potentiometrically using a fluoride-specific ion-selective electrode with a sealed reference electrode in a double-junction configuration. The operation of the fluoride electrode is based upon the potential that develops across a crystal lanthanum fluoride membrane. This potential is proportional to the activity of fluoride ions in contact with the membrane. The fluoride ion activity is related to the free fluoride concentration per Equation 1.

EQUATION 1

$$A = (\gamma) \times (c)$$

Where:

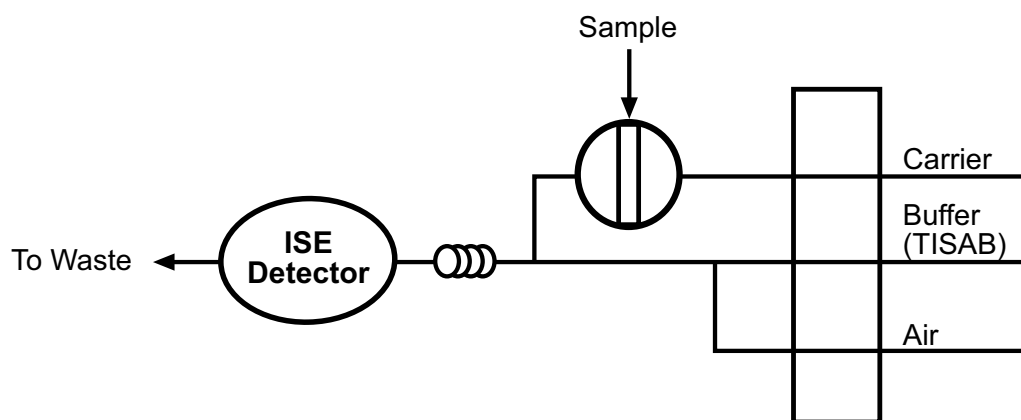
A = Activity

γ = Activity coefficient

c = Concentration

The activity coefficient is estimated from the total quantity of ions in solution or the ionic strength. A total ionic strength adjusting buffer (TISAB) is used to stabilize the ionic strengths of the samples at high levels, making their activity coefficients essentially the same.

- 2.2 The quality of the analysis is assured through reproducible calibration and testing of the Flow Injection Analysis (FIA)/Segmented Flow Analysis (SFA) system.
- 2.3 A general flow diagram of the FIA/SFA system is shown below (see Section 17.0 for a detailed flow diagram).



3.0 Definitions

Definitions for terms used in this method are provided in Section 16.0, "Glossary of Definitions and Purposes."

4.0 Interferences

- 4.1 Cations and most anions do not interfere with the response of the fluoride electrode to fluoride ions. Anions commonly associated with fluoride, such as chloride, bromide, iodide, sulfate, bicarbonate, nitrate, phosphate, and acetate, do not interfere with the electrode operation.
- 4.2 Polyvalent cations of silicon(IV), iron(II), and aluminum(III) interfere by forming complexes with fluoride. The amount of interference depends upon the concentrations of the complexing cations, the concentration of fluoride, and the pH of the sample. Eliminate this interference by adding 1,2-cyclohexylenedinitrilotetraacetic acid monohydrate (CDTA) to the TISAB to bind the complexing metal ions. In a sample containing 1 mg/L fluoride, CDTA binds approximately 3–5 mg/L aluminum or iron.
- 4.3 Hydroxide ion is an electrode interferant. Anions such as carbonate and phosphate make the sample more basic, increasing the hydroxide interference. Eliminate this interference by buffering the sample to pH 5.0–5.5 using the TISAB (Reference 15.4).
- 4.4 In solutions with pH <5, hydrogen ions complex with fluoride, forming a poorly ionized hydrogen fluoride complex (HF–HF). Buffer the sample to pH 5.0–5.5 to eliminate this interference (Reference 15.4).

- 4.5 Since electrode potentials are affected by temperature changes, samples and standards should be as close as possible to the same temperature. A 1°C change in temperature can cause up to a 2% error in the fluoride results. The slope of the fluoride electrode also varies with temperature.

5.0 Safety

- 5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been fully established. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.
- 5.2 For reference purposes, a file of Material Safety Data Sheets (MSDS) for each chemical used in this method should be available to all personnel involved in this chemical analysis. The preparation of a formal safety plan is also advisable.
- 5.3 The following chemicals used in this method may be highly toxic or hazardous and should be handled with extreme caution at all times. Consult the appropriate MSDS before handling.
- 5.3.1 Acetic Acid, glacial, $C_2H_4O_2$ (FW 60.05)
 - 5.3.2 1,2-Cyclohexylenedinitrilotetraacetic Acid Monohydrate (CDTA), $C_6H_{10}[N(CH_2CO_2H)_2]_2 \cdot H_2O$ (FW 364.36)
 - 5.3.3 Kleenflow™ Basic (Part #A002294)
 - 5.3.4 Sodium Chloride, NaCl (FW 58.44)
 - 5.3.5 Sodium Fluoride, NaF (FW 41.99)
 - 5.3.6 Sodium Hydroxide, NaOH (FW 40.00)
- 5.4 Unknown samples may be potentially hazardous and should be handled with extreme caution at all times.
- 5.5 Proper personal protective equipment (PPE) should be used when handling or working in the presence of chemicals.
- 5.6 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

6.0 Apparatus, Equipment, and Supplies

- 6.1 Flow Injection Analysis (FIA)/Segmented Flow Analysis (SFA) System (OI Analytical Flow Solution® IV) consisting of the following:
- 6.1.1 Model 502 Multichannel Peristaltic Pump

- 6.1.2 Random Access (RA) Autosampler
- 6.1.3 Data Acquisition System (PC or Notebook PC) with WinFLOW™ software
- 6.1.4 Fluoride by ISE Cartridge (Part #A002677), which includes:
 - 6.1.4.1 Expanded Range (ER) Potentiometric Detector
 - 6.1.4.2 Combination Fluoride ISE
- 6.1.5 For FIA, Flow Solution IV must be equipped with the FIA option.
- 6.2 Sampling equipment—Sample bottle, high density polyethylene (HDPE), with polytetrafluoroethylene (PTFE)-lined cap. Clean by washing with detergent and water, rinsing with two aliquots of reagent water, and air drying on a rack.
- 6.3 Standard laboratory equipment including volumetric flasks, pipettes, syringes, etc. should all be cleaned, rinsed, and dried per bottle cleaning procedure in Section 6.2.

7.0 Reagents and Calibrants

7.1 Raw Materials

- 7.1.1 Acetic Acid, glacial, $C_2H_4O_2$ (FW 60.05)
- 7.1.2 Brij®-35, 30% w/v (Part #A21-0110-33)
- 7.1.3 1,2-Cyclohexylenedinitrilotetraacetic Acid Monohydrate (CDTA), $C_6H_{10}[N(CH_2CO_2H)_2]_2 \cdot H_2O$ (FW 364.36)
- 7.1.4 Deionized Water (ASTM Type I or II)
- 7.1.5 Kleenflow Basic (Part #A002294)
- 7.1.6 Sodium Chloride, NaCl (FW 58.44)
- 7.1.7 Sodium Fluoride, NaF (FW 41.99)
- 7.1.8 Sodium Hydroxide, NaOH (FW 40.00)

7.2 Reagent Preparation

Note: For best results, filter and degas all reagents prior to use. Avoid the use of glass-distilled water. Immediately after preparation, transfer all reagents and calibrant solutions to polyethylene containers.