

## METHOD 24

REF: Reg 10-1-301  
12-5-301

### DETERMINATION OF TOTAL FLUORIDE IN EFFLUENTS

#### 1) PRINCIPLE

1.1 Gaseous and water soluble particulate fluorides are collected in a dilute alkaline solution. The absorbed fluorides are quantified by the use of a fluoride specific ion meter. A buffer solution containing a chelating agent is used to prevent possible interferences from aluminum, iron and hydroxyl ions.

#### 2) APPARATUS

2.1 Orion specific Ion Meter (Model 407 A).

2.1.1 Sleeve-type Reference Electrode (Orion No. 90-01-00).

2.1.2 Fluoride Ion Electrode (Orion No. 94-09).

2.2 Magnetic Stirrer and Teflon Stirring Bar (2.5 cm).

2.3 Polyethylene Beakers, 100 ml

2.4 Polyethylene 1 liter Volumetric Flask.

#### 3) REAGENTS

3.1 Sodium Fluoride.

3.2 Total Ionic Strength Adjustment Buffer (TISAB).

3.2.1 Dissolve 228 ml of glacial acetic acid, 232 g of sodium chloride and 4 g of CYTA (1,2, cyclo-hexylene-dinitrilo) Tetraacetic Acid in a 4 liter beaker containing approximately 2000 ml of distilled water.

**3.2.2** Slowly add, with stirring, 160 ml of 50% sodium hydroxide solution while cooling the beaker in an ice bath. Allow the solution to come to room temperature and adjust the pH to between 5.0 and 5.5 using 50% sodium hydroxide solution.

**3.2.3** Transfer the solution into a 4 liter bottle and bring to volume with distilled water.

**3.3 Sodium Hydroxide Solution (0.1 N).** Dissolved 4.0 g of sodium hydroxide pellets in 1 liter of distilled water.

#### 4) ANALYTICAL PROCEDURE

**4.1** Measure and record the total volumes of each impinger.

**4.2** Transfer a 15.0 ml aliquot of sample to a 100 ml polyethylene beaker containing a teflon stirring rod, and add 15.0 ml of the TISAB solution.

**4.3** Calibrate the ion meter as described in **Section 6**.

**4.4** Immerse the ion meter electrodes into the prepared sample and stir the solution slowly. Record the  $\mu\text{g}$  fluoride reading after a constant reading has been obtained.

**4.5** All sample readings must be bracketed between the calibration standards. If the sample reads less than the 10  $\mu\text{g}$  F standard, report the result as traces.

**4.5.1** Sample readings greater than 10  $\mu\text{g}$  F must be diluted with a solution containing equal amounts of TISAB and 0.1 N sodium hydroxide to be in the range of the calibration standards. Alternately, a smaller aliquot of the impinger may be taken and brought to 15.0 ml with 0.1 N sodium hydroxide. Add 15.0 ml of TISAB and proceed as in **4.4**.

**4.6** The ion meter should be recalibrated periodically with the middle range calibration standard. Rechecking after every tenth sample has been found to be adequate.

#### 5) STANDARD PREPARATION

**5.1 Standard Stock Fluoride Solution.** Weigh and transfer 0.2210 g of sodium fluoride to a 1 liter volumetric flask. Dissolve in distilled water and bring to volume. This solution contains 100  $\mu\text{g}$  of fluoride ion per ml. The solution is stable for one year when stored in a plastic bottle.

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**5.2 Working Standard Fluoride Solutions.** Three standards, respectively 1.0, 5.0 and 10.0 µg F/ml are prepared by the appropriate dilution of the standard stock fluoride solution with distilled water. These standards if stored in plastic bottles are stable for six months.

## 6) CALIBRATION OF THE ION METER

**6.1** Prepare three calibration fluoride solutions containing 1.0, 5.0 and 10.0 µg as follows:

**6.1.1** The 1.0 µg calibration standard is made by pipetting 1.0 ml of the 1.0 µg F/ml standard **(5.2)** into a 100 ml polyethylene beaker and adding 14.0 ml of 0.1 N sodium hydroxide.

**6.1.2** The 5.0 µg calibration standard is made by pipetting 0.5 ml of the 10.0 µg F/ml standard **(5.2)** into a 100 ml polyethylene beaker and 14.5 ml of 0.1 N sodium hydroxide.

**6.1.3** The 10.0 µg calibration standard is made by pipetting 1.0 ml of the 10.0 µg F/ml standard **(5.2)** into 100 ml polyethylene beaker and adding 14.0 ml of 0.1 N sodium hydroxide.

**6.2** The ion meter is calibrated using the three calibration standards (6.1.1 - 6.1.3), each with 15.0 ml of TISAB having been added, as described in the instrument manual. It is important to maintain a constant slow stirring rate when the electrodes are immersed in the calibration solutions. Rinse the electrodes and blot dry with clean tissue between readings to prevent solution carry over.

## 7) CALCULATIONS

**7.1**        \* 
$$\text{Total } \mu\text{g F} = \frac{(\mu\text{g F, Meter Reading})(\text{Impinger Vol. ml})}{\text{Aliquot (ml)}}$$

\* If the sample was diluted to be within the calibration standards, the calculation must be multiplied by the appropriate dilution factor

**7.2**        
$$\text{Total } \mu\text{g F} = \mu\text{g F Imp I} + \mu\text{g F Imp II}$$

## REFERENCE

- 8.1 Orion analyzer Instruction Manual for Model 407 A. Orion Research Inc., Cambridge, Mass.
- 8.2 40 CFR 60.275 Appendix A, Method 13 B. **"Determination of Total Fluoride Emissions from Stationary sources - Specific Ion Electrode Method"**.