

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 μg 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 μg F standard, report the result as traces.

4.5.1 Sample readings greater than 10 μg 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 μg of fluoride ion per ml. The solution is stable for one year when stored in a plastic bottle.

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"**.