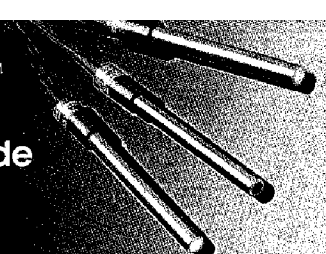


# IOTRODE™

## Ion-Selective Electrode Applications



Bulletin No. 000418

### Fluoride Analysis In Acid Baths

#### INTRODUCTION

The following procedure is provided as a general method for determining fluoride levels in chromic, nitric, hypochloric, perchloric, and other strong acids. The major requirement for sample preparation is sodium acetate or sodium citrate be added to free the fluoride ion and adjust both pH and ionic strength.

#### EQUIPMENT

**Meter:**  
pH/Millivolt meter. Readability of 1 mV required; 0.1 mV preferred. Specific ion meter will provide direct readout of final answer or concentration factor. Consult manual for millivolt measurement instructions.

**Electrodes:**  
Measuring Electrode: Iotrode AB-100 Fluoride ISE.  
Reference Electrodes—Double Junction—Refillable  
Calomel — RD-101 Removable Sleeve  
                  RD-201 Non-Removable Sleeve  
Ag/AgCl — RD-301 Removable Sleeve  
                  RD-401 Non-Removable Sleeve

#### Glassware:

1. 1 ml, 2 ml, and 10 ml pipets
2. 150 ml beakers
3. 100 ml graduated cylinders
4. 100 ml, 1000 ml volumetric flasks
5. Magnetic stirrer and stirbars or glass stirring rods

#### REAGENTS

- 1. Sodium Acetate Buffer (SAB):** Weigh out 150 grams of sodium acetate into a one liter volumetric flask. Dilute to mark with deionized water.
- 2. Sodium Hydroxide (15%):** Add 15 grams of solid sodium hydroxide to a 100 ml volumetric flask. Dilute to mark with deionized water.
- 3. Sodium Citrate Buffer (SCB):** Weigh out 150 grams of sodium citrate into a one liter volumetric flask. Dilute to mark with deionized water.
- 4. Fluoride Standard:** The fluoride standard should be approximately 100 times the sample concentration. Use sodium fluoride to prepare standard. To prepare a 100 ppm fluoride standard, dissolve 0.221 grams NaF in deionized water and dilute to one liter.  
Reference Electrode Outer Junction Filling Solution: Weigh out 10 grams KNO<sub>3</sub> and dilute to 100 ml with deionized water.

#### ELECTRODE SET-UP

Plug the sensing electrode into the G.E. or Glass jack of the meter. Fill the inner and outer chambers of the reference electrode with appropriate solutions (refer to reference electrode instructions). Plug the reference electrode into the REF or Reference jack of the meter.  
Technique Hints:

1. **Stirring:** Electrode response is improved if samples and standardizing solutions are stirred at a fixed rate during measurements. If magnetic stirring is not available, stir solution one minute with a clean glass stirring rod before measuring.
2. **Temperature:** The slope of the sensing electrode and the absolute potential of the reference electrode are temperature dependent. Therefore, samples and standardizing solutions should be at the same temperature.
3. **Cleaning Electrodes:** Rinse both electrodes with a fresh portion of deionized water and blot dry with tissue between all measurements.

#### ELECTRODE CALIBRATION

The primary criterion for electrode performance verification is the span test. If 55 millivolts or greater change is observed for a decade change in concentration, the performance is considered satisfactory.

1. Put 100 ml deionized water and 2 ml ISA into a 150 ml beaker. Place the pH meter into the MV mode. Place electrodes in the solution to a minimum depth of one inch.
2. Pipet 1 ml of fluoride standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E1.
3. Add 10 ml of fluoride standard and stir thoroughly. Read stable electrode potential in millivolts and record as E2. Calculate S by E2-E1. Assume S value as the slope of the electrode.

NOTE: If the slope value is below 55 mV, check electrode set-up.

**PROCEDURE**

**Sample Preparation:** For samples without metal complexes, add 90 ml of SAB to 10 ml of sample solution and adjust pH to above 5 with 15% NaOH.

For samples with metal complexes, add 90 ml of SCB to 10 ml of sample and adjust pH to above 5 with 15% NaOH.

**Sample Standardization:** Add 100 ml of prepared sample to a 150 ml beaker. Place electrodes in the solution to a minimum depth of one inch. Read stable electrode potential in millivolts and record as E3.

**Standard Addition:** Pipet 1 ml of fluoride standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E4. Calculate  $\Delta E$  by  $E4 - E3$ .

NOTE: If  $\Delta E$  is more than 30mV, **dilute standard** 1:10 with deionized water and divide final concentration by 10. If  $\Delta E$  is less than 8mV, **dilute fresh sample** 1:10 with deionized water and multiply final concentration by 10.

**CALCULATIONS**

To perform the calculation for standard addition, the following factors are needed:

- $V_s$  = Sample Volume
- $V_a$  = Volume of standard added
- $C^*$  = Concentration of standard
- $\Delta E$  = Change in potential (see procedure section)
- $S$  = Slope of the electrode (see electrode calibration section)

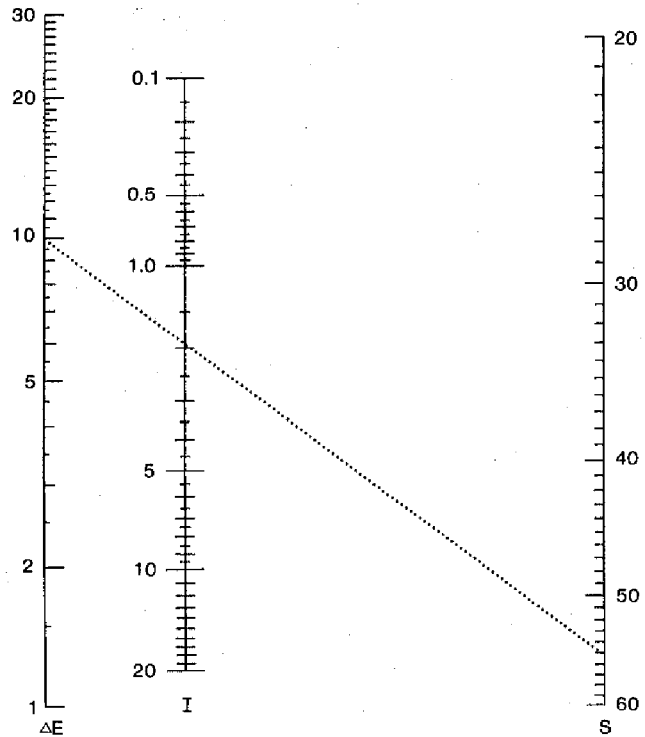
$$\text{Concentration of Sample} = \frac{C^* \left[ \frac{V_a}{V_a + V_s} \right]}{\left[ \text{antilog} \frac{\Delta E}{S} \right] - \left[ \frac{V_s + V_a}{V_s} \right]}$$

Note: If the sample is diluted, multiply sample concentration by appropriate dilution factor.

**REFERENCES:**

Hanson, W. C. and Lloyd, D. J., "Direct Determination of Fluoride in Phosphoric Acid and Calcium Sulfate Using a Specific Ion Electrode, Chem. and Ind. 41 (1972).

**Standard Addition Nomograph for use with Iotrode™ Electrodes**



The standard addition nomograph method of calculation is valid when the increment of standard added to the sample is small compared to the volume. Therefore, if more than 1 ml of standard is added, please utilize the mathematical procedure above.

The following data must be known to utilize the nomograph: (See above for description of factors.)

$\Delta E$ ,  $S$ ,  $C^*$ , and  $V_s$

Utilizing  $\Delta E$  and  $S$ , draw a straight line to find  $I$  on the nomograph.

$$\text{Concentration of Sample} = \frac{(I)(C^*)}{V_s}$$

The concentration of Sample will be in the same units of concentration as  $C^*$ .

- Example:  $\Delta E = 10$  mv
- $S = 55$  mv
- $C^* = 1000$  ppm
- $V_s = 100$  ml
- $I = 2.0$  (from Nomograph)

$$\begin{aligned} \text{Sample Concentration} &= \frac{(2.0)(1000 \text{ ppm})}{100 \text{ ml}} \\ &= 20 \text{ ppm} \end{aligned}$$