

8.1.03

AOAC Official Method 973.10 Fluorides in Hazardous Substances

Potentiometric Method First Action 1973 Final Action 1975

A. Apparatus

(a) *pH meter*.—With expanded mV scale (Model 250, Nova Analytics Corp., 6E Gill St, Woburn, MA 01801, USA; www.novaanalytic.com; or equivalent), fluoride ion-selective electrode (Model 940900, Orion Research, Inc., available through ThermoElectron Corp., Waltham, MA 02454, USA; www.thermo.com, or equivalent), and single junction reference electrode, plastic sleeve-type (Model 900100, Orion Research Inc., or equivalent; or Orion combination electrode 960900).

(b) *Magnetic stirrer*.—With PTFE-coated stirring bar. Use foam mat to insulate sample from motor heat.

(c) *Beakers*.—150 mL polypropylene, or equivalent.

(d) *Graph paper*.—Linear or semi-antilog, volume corrected No. 90-00-90 Gran's plot paper (Orion Research Inc., or equivalent).

B. Reagents

(a) *Buffer solution*.—pH 6.0. Add 77.0 g ammonium acetate and 0.452 g ammonium citrate to 1 L H₂O. Adjust to pH 6.0 with ammonium acetate.

(b) *Sodium fluoride standard solution*.—1 mg F⁻/mL (reagent grade, dried 4 h at 105°C). Prepare NaF, 2.2108 g/L, in buffer solution. Store in plastic bottles. Compare with 1 mg F⁻/mL solution prepared from USP Reference Standard; equivalent reading of 1 mV is satisfactory.

C. Determination

(Stir all solutions constantly at same rate throughout titrations. Let electrodes equilibrate 2 min before adding F⁻ standard solution and 30 s after each addition of F⁻ standard solution.)

(a) *Blank*.—Record mV values (E) of 100 mL buffer solution after addition of 4 mL standard F⁻ solution from 10 mL buret and after each additional mL up to 10 mL. (Preliminary mV values will not fall on linear range of response curve.) Volume standard solution added = V .

(b) *Test solutions*.—Estimate molarity of test solutions from direct reading. Dilute test solutions, if necessary, to ca 0.001M F⁻. Transfer 50 mL test solution to beaker and add 50 mL buffer

solution. Record initial mV reading (E_0). If initial reading is <-50 mV, solution is too concentrated. Dilute test solution to avoid asymptotic slope. Record mV reading (E) after each mL F⁻ standard solution added, up to 10 mL. Rinse electrodes with H₂O between test solutions. Volume standard solution added = V .

D. Calculations

(a) *Linear graph paper*.—For each addition of F⁻ standard solution and corresponding E value, calculate for blank:

$$Z = \text{antilog} [\log(V_0 + V) - 0.017(E)]$$

where V_0 is original volume of solution to which F⁻ standard solution was added (100 mL). E is treated algebraically (+ or - as read). Plot Z against mL (or mg) F⁻ standard solution added and extrapolate plot to F⁻ axis to obtain mL F⁻ in blank, V_e . On graph, assign x axis to mL F⁻, with 0 at center of axis and mL F⁻, increasing in both directions to left and right. Plot experimental readings of mL F⁻ on right portion of horizontal axis so that extrapolation is performed on left portion of axis.

Similarly, calculate for test solution:

$$Z = \text{antilog} [\log(V_0 + V) - 0.017(E)]$$

where V_0 is original volume solution to which F⁻ standard solution was added (100 mL). Plot Z against mL (or mg) F⁻ standard solution on same graph as blank and extrapolate to mL F⁻ axis obtaining mL F⁻ in test solution, V_e .

(b) *Semi-antilog paper*.—Plot E versus V_e directly for both blank and test material (scale E at 5 mV for each major grid line crossing Y axis). Begin plot with most negative E reading that allows extrapolation of V_e on left portion of mL F⁻ axis. Obtain V_e and V_e by extrapolation to left side of 0 mL (mg) F⁻.

$$F, \% = \frac{(V_e - V_e) (B - 100)}{W C 1000(\text{mg/g})}$$

where B = volume of dilution, W = mL or g test solution, and C = aliquot (50 mL maximum) buffered to 100 mL.

Reference: *JAOAC* **56**, 798(1973).

CAS-7782-41-4 (fluorine)