

Thermo. Titr. Application Note No. H-098

Title: Determination of Hydrofluoric Acid in Silicon Etch solutions

Scope: Determination of fluoride in industrial solutions such as acid etching mixtures.

Principle: Acidic solutions of fluoride react exothermically with boric acid according to the equations:

$$\text{H}_3\text{BO}_3 + 3\text{H}^+ + 3\text{F}^- \leftrightarrow \text{HBF}_3(\text{OH}) + 2\text{H}_2\text{O} \quad (1)$$
$$\text{HBF}_3(\text{OH}) + \text{H}^+ + \text{F}^- \leftrightarrow \text{HBF}_4 + \text{H}_2\text{O} \quad (\text{slow}) \quad (2)$$
$$\text{H}_3\text{BO}_3 + 4\text{H}^+ + 4\text{F}^- \leftrightarrow \text{HBF}_4 + 3\text{H}_2\text{O}$$

When fluoride is the analyte (and boric acid the titrant), only reaction (1) is observed, and hence 3 mol of fluoride reacts with 1 mol of boric acid.

The titrations are carried out in plastic titration vessels (e.g., 6.1450.210 PFA titration vessel, 10-90mL), as acidic fluoride solutions react with glass vessels. A fluoride-resistant 6.9011.040 Thermoprobe is also used in this determination.

Reagents: 0.7 mol/L boric acid solution

Method:

Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	2.5
No. of endothermic endpoints	1
Data smoothing factor	80

Procedure:

An aliquot of sample solution is weighed into a titration vessel. D.I. water is added to make the volume to ~30mL. The solution is titrated with standard H₃BO₃ solution to a single exothermic endpoint. The titration program includes a 120 second delay under stirring before titrant addition commences. This ensures a satisfactory equilibration of temperature.

The etch solution analysed here comprised a very

high proportion of nitric acid with a small amount of hydrofluoric acid. An average sample mass of approximately 20g was employed.

Results:

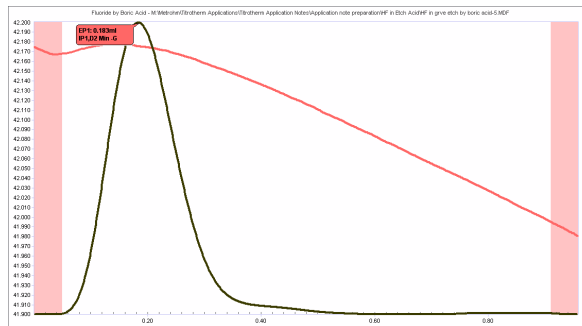
Replicate analysis of a used etch solution from etching of silicon substrate:

% HF = 0.049, 0.047, 0.047, 0.046

Calculation:

$$\%HF = \frac{((\text{titre, mL} - \text{blank, mL}) \times M_{H_3BO_3} \times FW_{HF} \times 3 \times 100)}{(\text{sample vol, mL} \times 1000)}$$

Thermometric Titration Plot:



Legend:

Red = solution temperature curve

Black = second derivative curve

Blank determination

Note: the less than ideal linearity is a function of the extremely small titration volumes (~0.14 – 0.24mL) experienced when analyzing the sample. However, the fact that the titration volume was seen to vary with sample mass shows the validity of the method in analyzing small amounts of HF

