



Overview The concentration of ammonium bifluoride, nitric acid, and free acid* in etching bath is determined by performing a series of two multiple known addition (MKA) analyses on the Orion 960 Titrator and using results to manually calculate the amount of each species. This method is better than analysis of free acid by acid-base titration, since not necessary to remove interfering heavy metal ions. This log describes the analysis of fluoride by MKA using the Orion fluoride electrode and fluoride standard and the calculation required to determine the percent concentration of the species listed above.

Market Metals

Species Measured Ammonium bifluoride; free acid

Sample Etching bath

Sample Size 0.2mL

Typical Concentration NH₄HF₂=1.9%; Free acid=37%

Technique # 2 Multiple Known Addition

Electrode Ionplus® fluoride electrode (Orion 9609BNWP)

Solutions 0.1M Sodium Fluoride Standard (Orion 940906); Optimum Results A filling solution (Orion 900061); TISAB II (Orion 940909); deionized water (DI).

Solutions preparation: Use Orion prepared solutions.

Titration standardization: Fluoride standard is already standardized.

Sample Prep Pipette 20 mL of DI water and 20 mL TISAB into titration beaker. Accurately pipette 0.2mL of sample into this mixture.

Statistics

of Trials 4 **Mean** See page 2 **%CV** **Analysis Time** 3 minutes

Comments *Free acid is defined as the amount of inorganic acid in the etching solution. This term has been introduced to differentiate the inorganic acid from heavy metal ions which act as acids due to the hydrolysis. Free acid is usually analyzed using alkalimetric titration after sample is pretreated, which removes the hydrolysable metal ions. This method allows for the measurement of free acid, nitric acid, and ammonium fluoride without removing the metal ions. See calculation on page 2.

Method Parameters

Sample Volume/Weight	0.2 mL	Timed or Stability Readings	3.0mV/min stability
Constant Increment	18 mV	Number of Endpoints	n/a
Max Titrant Volume	10 mL	Desired Units	M
Molecular weight	n/a	Predose	none
Prestir	1 sec.	Additional Parameters	Total solution volume = 40.2 mL; Precision 2%
Reaction Ratio	1		



Results

METHOD 1 SUMMARY

SAMPLE ID NUMBER: 10
 TEST:
 0.2mL of AC-4 (etching solution sample) +20mL
 DI+20mL TISAB II; pH=4.95
 SITE: _____
 ANALYST: _____
 12:24 04-30-08 ELECTRODE: 1:F-
 TECHNIQUE 2 MULTIPLE KNOWN ADDN
 TOTAL SOLN VOL 40.200 mL
 SAMPLE VOLUME 0.200 mL
 STANDARD .1000 M of F^- Standard
 PRECISION 2.0 %
 CONST INCREMENT 18.0 mV
 MAX STANDARD VOL 10.000 mL
 STABILITY CRITERION 3.0 mV/min
 PRESTIR 1.0 sec
 CONTINUOUS STIRRING
 REACTION RATIO 1.0000
 CAL CONSTANT 1.06635

electrode check: +/- 0.0 mV
 ok
 0 v= 0.000 mL E= -22.9 mV 11 sec
 -0.6 mV/min drift +/- 0.0 mV noise
 1 v= 1.013 mL E= -36.9 mV 39 sec
 0.0 mV/min drift +/- 0.0 mV noise
 unkn=.661
 2 v= 5.278 mL E= -60.9 mV 45 sec
 -0.0 mV/min drift +/- 0.0 mV noise
 S= -58.3 Eo=-168.2 unkn=.649
 3 v= 10.024 mL E= -72.4 mV 34 sec
 -1.9 mV/min drift +/- 0.0 mV noise
 S= -59.1 Eo=-169.6 unkn=.664
 std dev= 0.0 mV precn= 2.2 %

2.8 min

MULTIPLE INCREMENT ANALYSIS

SAMPLE = .664 M +/- 2.2%
 SPIKE RECOVERY= 100.4%
 RECOVERY ERROR= 0.4%

Calculation of the percent concentration of ammonium bifluoride and free acid

- $C_{NH_4HF_2}, \% = (MW_{NH_4HF_2} * M_F) / 20$
 Where:
 $C_{NH_4HF_2}, \%$ - ammonium bifluoride concentration, % (w/v)
 $MW_{NH_4HF_2}$ - 57g/mole
 M_F - molar concentration of F^- (determined by MKA)

Example of calculation:
 $C_{NH_4HF_2}, \% = (57 * 0.664) / 20 = 1.9\%$

- Free acid is calculated as a sum of nitric and hydrofluoric Acids

- $C_{HF}, \% = (MW_{HF} * M_F) / 20$
 Where:
 $C_{HF}, \%$ = HF concentration, % (w/v)
 MW_{HF} - 20 g/mole
 M_F - molar concentration of F^- (determined by MKA)

Example of calculation:
 $C_{HF}, \% = (20 * 0.664) / 20 = 0.7\%$

- $C_{free\ acid} = C_{HNO_3} + C_{HF}$
 Where:
 $C_{free\ acid}$ = free acid concentration, % (w/v)
 C_{HNO_3} - percent concentration of nitric acid, % w/v (from Applications Log 712A)
 C_{HF} - percent concentration of hydrofluoric acid, %w/v

Example of calculation:
 $C_{free\ acid} = 36.5 + 0.7 = 37.2\%$

Note: Ammonium bifluoride dissociates in water to hydrofluoric acid and fluoride ion. The concentration of free fluoride is a function of the pH of the solution. After a sample pretreatment, which is described on page 1, each molecule of ammonium bifluoride releases two fluoride ions, due to high pH of solution after pretreatment.