Thermo. Titr. Application Note No. H-114

Title:	**Determination of sulfuric acid, nitric acid, and hydrofluoric acid in etch solutions**

***Scope*:**	Determination of sulfuric acid, nitric acid, and hydrofluoric acid etch solutions.

***Principle*:**	Two separate titration sequences are required to analyze the mixture: - titration of the HF content with $Al(NO_3)_3$ (the "elpasolite" reaction) - titration of the H_2SO_4 with $BaCl_2$ followed by titration with NaOH to determine the "total acids" content The HF, H_2SO_4, and "total acids" contents are converted to a HNO_3 equivalent, with the HNO_3 content found by subtracting the HF and H_2SO_4 from the "total acids" content.

Reagents:	*Titrant #1*: 0.5 mol/L $Al(NO_3)_3$ in D.I. water *Titrant #2*: 1 mol/L $BaCl_2$ in D.I. water *Titrant #3*: 2 mol/L NaOH *Standard #1:* Anhydrous A.R. NaF, 99% *Standard #2:* Anhydrous A.R. Na_2SO_4, 99.9% *Standard #3:* A.R. potassium hydrogen pthalate, 99.95% *pH 4.5 buffer solution.* Weigh 130.9 g anhydrous potassium acetate, and 54.7 g anhydrous acetate and dissolve in 600 mL deionized water. Add 115 mL glacial acetic acid, and make to 1000 mL with deionized water.

Method:	*Basic equipment list (for automated titration):* *859 Titrotherm interface* *814 Sample Processor with 24 place rack, 75 mL PP tubes* *802 Magnetic Stirrer with propeller mixer* *800 Dosinos,* 1 x 5 mL, 3 x 10 mL burettes *6.9011.040* Thermoprobe (fluoride resistant) *Basic experimental parameters:* *HF titration* Sample size (g): ~3 Titrant delivery rate (mL/min) 4 ERC (exothermic) -10 Data smoothing factor 53 Stirring speed (802 Magnetic Stirrer) 12

H_2SO_4 titration

Titrant delivery rate (mL/min)	4
ERC (exothermic)	-25
Data smoothing factor	50
Stirring speed (802 Magnetic Stirrer)	14

"total acids" titration

Titrant delivery rate (mL/min)	4
ERC (exothermic)	-150
Data smoothing factor	50
Stirring speed (802 Magnetic Stirrer)	15

Methods:
NOTES:

(a) In each of the following methods, the HF titration must precede the H2SO4-"total acids" titration

(b) Due to the concentrated nature of the solution, use of an "air pipette" to dispense accurate aliquots is not recommended. In the case of an accurate auto-diluter not being available, it is permissible to weigh in the samples, correcting the sample mass to a volume equivalent via a previously determined density of the sample.

1. HF titration
When installing the method for the first time, create a CV to hold the result for HF g / L. Dispense accurately 2 mL of sample solution into a plastic titration vessel, add 5 mL D.I. water, and add 30 mL acetate buffer, either automatically via a Dosino or by auto dilution. Titrate with the HF titration method.

2. H_2SO_4/total acids titrations
Dispense accurately 1 mL of sample solution into a plastic titration vessel, and add 30 mL D.I. water. Titrate with the H_2SO_4 "total acids" method.

3. *Determination of blank for HF titration*
When installing the method for the first time, prepare a CV for the HF titration blank. Prepare at least 5 plastic titration vessels, with dispensing volumes ranging from 0.5 to 2 mL of etch solution. Add 5 mL D.I. water and 30 mL acetate buffer. Titrate with the HF titration blank method.

4. *Determination of blanks for H_2SO_4 and "total acids" titrations*
When installing the methods for the first time, create CVs for the H_2SO_4 and "total acids" blanks. Prepare at least 5 plastic titration vessels, dispensing volumes of sample

ranging from 0.2 to 1.0 mL. Titrate with the H_2SO_4/"total acids" titration blank method.

5. Standardization of 0.5 mol/L $Al(NO_3)_3$ titrant
Prepare at least 5 plastic titration vessels, weighing in accurately approximately 0.25 to 0.6 g freshly dried anhydrous NaF in roughly even increments. Add 5 mL acetate buffer and 25 mL water. Titrate with the $Al(NO_3)_3$ standardization method.

6. Standardization of 1 mol/L $BaCl_2$ titrant
Prepare at least 5 plastic titration vessels, weighing in accurately approximately 0.14 to 0.85 g freshly dried anhydrous A.R. Na_2SO_4 in roughly even increments. Add 5 mL 5 mol/L HNO_3 and 25 mL D.I. water. Titrate using the $BaCl_2$ standardization method.

7. Standardization of 2 mol/L NaOH titrant
Prepare at least 5 plastic titration vessels, weigh in accurately approximately 0.4 to 2.4 g freshly dried A.R. potassium hydrogen phthalate in roughly even increments. Add 30 mL D.I. water, and titrate using the NaOH standardization method.

Results:

Analysis of a synthetic H_2SO_4-HNO_3-HF mixture

	H_2SO_4	*HF*	*HNO_3*
Mean, g/L	430.4	37.1	287.9
Std. dev. g/L	0.5	0.1	0.7
% RSD	0.11	0.22	0.24

Calculations:

HF titration:

HF g/L = ((EP mL-HF blank, mL)*$Al(NO_3)_3$ mol/L*FW HF*6/sample volume, mL

Conversion to HNO_3 g/L equivalent:

HNO_3 g/L equivalent = HF g/L*FW HNO_3/FW HF

H_2SO_4 "total acids" titrations

H_2SO_4 g/L = ((EP mL - H_2SO_4 blank, mL)*$BaCl_2$ mol/L*FW H2SO4)/sample volume, mL

Conversion to HNO_3 g/L equivalent:

Calculations

(continued)

HNO_3 g/L equivalent = H_2SO_4 g/L*2*FW HNO_3/FW H_2SO_4

"total acids" (as HNO_3) g/L = ((EP mL - "total acids" blank, mL)*NaOH mol/L*FW HNO_3/volume, mL

Titration Plots:

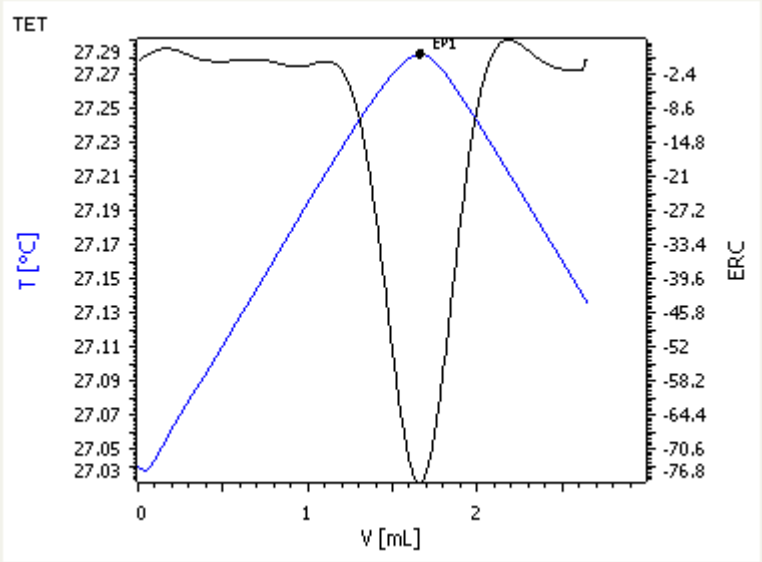

Fig. 1. Example of HF with Al titration plot

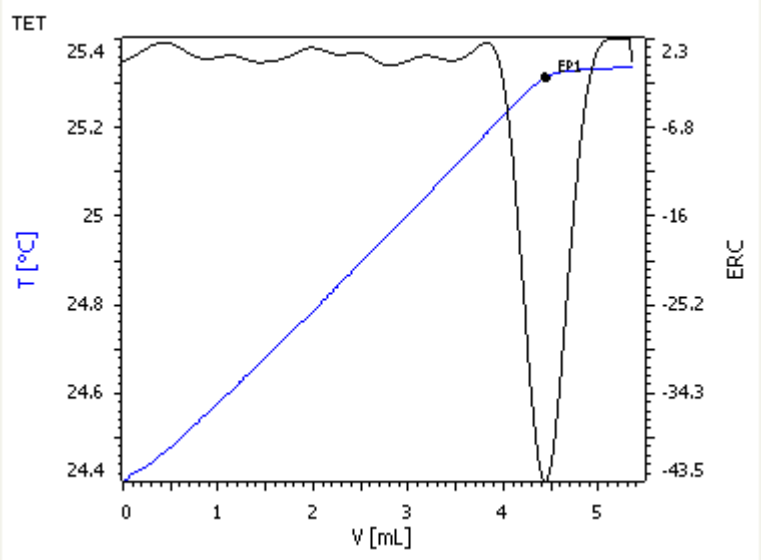

Fig. 2. Example of H_2SO_4 with $BaCl_2$ titration plot

Titration plots (continued)

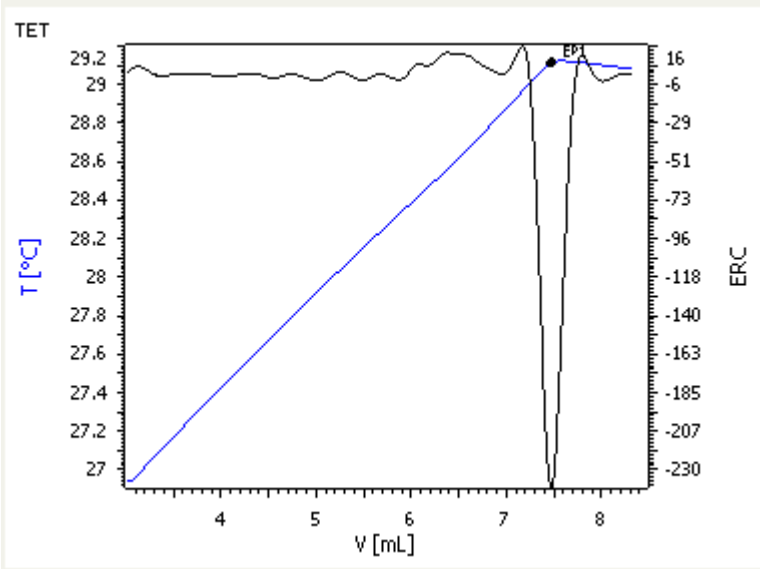

Fig. 3. Example of „total acids“ with NaOH titration plot