

Thermo. Titr. Application Note No. H-115

Title: Determination of hydrofluoric acid, ammonium fluoride, and maleic acid in acid cleaning solutions

Scope: Determination of hydrofluoric acid, ammonium fluoride, and maleic acid in cleaning solutions by thermometric titration (TET).

Principle: A direct TET with 2 mol/L NaOH is used to determine the HF, NH_4F , and maleic acid ($\text{C}_4\text{H}_4\text{O}_4$) contents of acid cleaning solutions. Three endpoints (EPs) are obtained, which may be assigned as follows:

EP1: $\text{C}_4\text{H}_4\text{O}_4$ ($\text{pK}_{\text{a}1} = 1.9$), HF ($\text{pK}_{\text{a}} = 3.17$)

EP2: $\text{C}_4\text{H}_4\text{O}_4$ ($\text{pK}_{\text{a}2} = 6.07$)

EP2: NH_4F ($\text{pK}_{\text{a}} = 8.2$)

The HF content is determined by subtracting the difference (EP2-EP1) from EP1.

Reagents: 2 mol/L NaOH, standardized against potassium hydrogen phthalate

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 Dosino, 1 x 10 mL burette
6.9011.040 Thermoprobe (fluoride resistant)

Basic experimental parameters:

Sample size (g):	~2
Titrant delivery rate (mL/min)	2
ERC EP1 (exothermic)	-40
ERC EP2 (exothermic)	-100
ERC EP2 (exothermic)	-25
Data smoothing factor	40
Stirring speed (802 Magnetic Stirrer)	14
Evaluation start (mL)	4
Damping until (mL)	4

Method:

Weigh accurately approximately 2 mL of acid cleaning mixture into a plastic titration vessel and add 30 mL D.I. water. Titrate to a third exothermic endpoint with 2 mol/L NaOH.

Note: Inflections for EPs 1 and 3 are weak. Some variation from those conditions listed here may be necessary with some setups.

Results:

Analysis of a synthetic HF-NH₄F-C₄H₄O₄ mixture (n = 7)

	HF	NH ₄ F	C ₄ H ₄ O ₄
Mean, %	8.87	3.72	3.18
Std. dev. %	0.05	0.03	0.13

Calculations:

$$\text{HF \%} = ((\text{EP1} - \text{blank, mL} - (\text{EP2} - \text{EP1})) * \text{NaOH mol/L} * \text{FW HF} * 0.1) / \text{sample mass, g}$$

$$\text{NH}_4\text{F \%} = ((\text{EP3} - \text{EP2}) * \text{NaOH mol/L} * \text{FW NH}_4\text{F} * 0.1) / \text{sample mass, g}$$

$$\text{C}_4\text{H}_4\text{O}_4 \% = ((\text{EP2} - \text{EP1}) * \text{NaOH mol/L} * \text{FW C}_4\text{H}_4\text{O}_4 * 0.1) / \text{sample mass, g}$$

Note: in the calculation of HF %, a blank value of 0.05 mL can be assumed for routine process control purposes.

Titration plots:

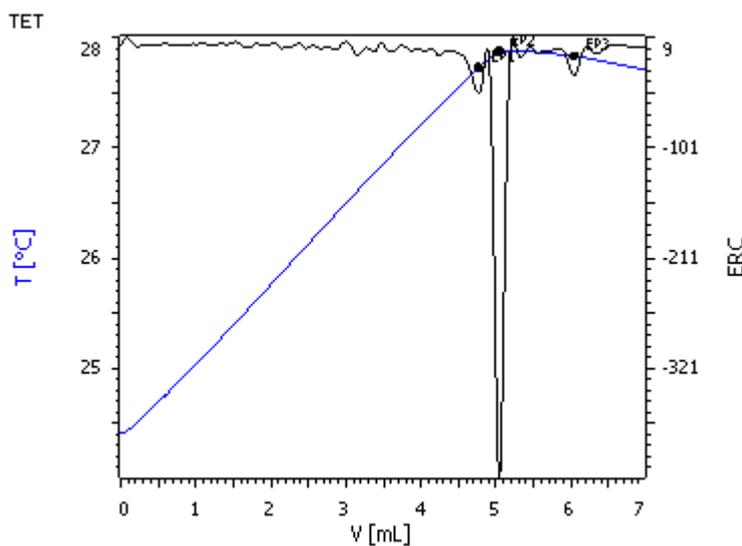


Fig. 1. Example of titration plot

Titration plots (cont.)

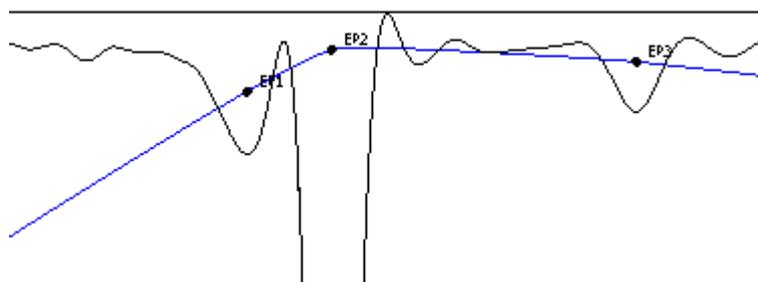


Fig. 2. Close-up of endpoint region of titration plot