Automated analysis of etch acid mixtures using the 859 Titrotherm and the 814 USB Sample Processor

Of interest to: solar cell industry, semiconductor industry

Summary

This bulletin deals with the automated determination of mixtures of HNO_3, HF and H_2SiF_6 in the range of approximately 200-600 g/L HNO_3, 50-160 g/L HF, and 0-185 g/L H_2SiF_6.

Etch acid mixtures containing HNO_3, HF and H_2SiF_6 from the etching of silicon substrates can be analyzed in a sequence of two determinations using 859 Titrotherm. The first determination involves a direct titration with standard c(NaOH) = 2 mol/L, followed by a back-titration with c(HCl) = 2 mol/L. This determination yields the H_2SiF_6 content plus a value for the combined (HNO_3+HF) contents. The second determination consists of a titration with c(Al^{3+}) = 0.5 mol/L to determine the HF content. Results from the two determinations are used by ***tiamo*™** to yield individual results for HNO_3, HF and H_2SiF_6.

For freshly made up mixtures of HNO_3 and HF containing no H_2SiF_6, a linked two titration sequence is employed. In the first titration, the combined HNO_3+HF content is determined with c(NaOH) = 2 mol/L. This titration is automatically stopped, and a titration with c(Al^{3+}) = 0.5 mol/L proceeds. Results from the linked titration sequence are used by ***tiamo*™** to yield individual results for HNO_3 and HF.

Introduction to thermometric titrations

In a titration, the titrant reacts with the analyte in the sample either exothermically (gives out heat) or endothermically (takes in heat). The Thermoprobe measures the temperature of the titrating solution. When all of the analyte in the sample has reacted with the titrant, the temperature of the solution will change, and the endpoint of the titration is revealed by an inflection in the temperature curve.

The amount of analyte determined is not related to the change in temperature of the solution. Therefore, it is not necessary to use insulated titration vessels.

Basic Theory

Thermometric titrations are conducted under conditions of constant titrant addition rate. In this respect they differ from potentiometric titrations, where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being given out or consumed, and hence a more or less constant temperature change up to the endpoint.

Apparatus and accessories

1 x	2.859.1010	859 Titrotherm (1 Dosino and 1 Dosing unit 10 mL included)
1 x	2.814.0030	814 USB Sample Processor
4 x	2.800.0010	800 Dosino
1 x	6.3032.150	Dosing unit 5 mL
1 x	6.3032.210	Dosing unit 10 mL
1 x	6.3032.220	Dosing unit 20 mL
1 x	6.1909.060	Stirring propeller (intensive)
22x	6.1459.300	PP sample tube 120mL
1 x	6.9914.159	Titration head
1 x	6.2041.470	Sample rack 22 x 120 mL
3 x	6.1805.030	FEP tubing M6 150 cm
1 x	6.2061.010	Reagent organizer
1 x	6.2065.000	Stacking frame

Equipment to dispense acid: The methods described here use small aliquots of the very concentrated acid etch solutions, typically ~1 mL. It is highly recommended to use a precision autodiluter for this work, and periodically maintain and calibrate it according to the manufacturer's instructions. A 1 mL "air pipette" can be used for non-critical work, but operators must be carefully trained and frequently monitored in its use. It should also be frequently maintained and calibrated. If a robotized titration system is to be used, a Dosino can be used as an autodiluter. Serial dilution using volumetric glassware should be avoided, due to the corrosive nature of the solutions.

Reagents

Solvent:	deionized water	
Standard (1):	Tris(hydroxymethyl)amino-methane ("TRIS")	
Standard (2):	c(NaF)	= 0.5 mol/L
Titrant (1):	c(NaOH)	= 2 mol/L
Titrant (2):	c(HCl)	= 2 mol/L
Titrant (3):	c($Al(NO_3)_3$)	= 0.5 mol/L
Buffer:	130.9 g anhydrous potassium acetate, 54.7 g anhydrous sodium acetate, 115 mL glacial acetic acid, made to 1000 mL with deionized water	

Samples

Synthetic samples were prepared from A.R. 70% w/v HNO_3, A.R. 48% w/v HF and ~19.2% H_2SiF_6 solution. Samples were prepared to aim for the following nominal concentrations:

Sample no.	HNO_3 g/L	HF g/L	H_2SiF_6 g/L
1	350	150	
2	420	115	
3	400	100	16
4	390	75	48
5	575	60	74
6	175	50	185

Calculations

Molarity determinations

The molarity of a titrant is computed from a regression analysis of titration results, where mmol of analyte (the standard) is plotted on the x-axis, and mL of titrant is plotted on the y-axis. This is computed automatically in ***tiamo***™, using the SLO command.

Molarity HCl

The molarity of HCl titrant is determined using a range of weighed quantities of TRIS. The basic calculation is:

c(HCl) mol/L = 1/slope x 1000/121.13504, where the formula mass of TRIS = 121.13504

Assignment	RS name	Formula
RS01	EP1 mL	'Molarity HCl with TRIS.EP{1}.VOL'
RS02	Slope	'RS.EP1 mL.SLO'
RS03	Intercept	'RS.EP1 mL.ITC'
RS04	Correlation	'RS.EP1 mL.COR' * 'RS.EP1 mL.COR'
RS05	Molarity	1/'RS.EP1 slope' * 1000/121.13504
RS06	mmol TRIS	'MV.Sample size' * 1000/121.13504

Molarity NaOH

The molarity of NaOH titrant is computed after titrating a range of volumes of standard HCl titrant:

c(NaOH) mol/L= c(HCl) mol/L/slope

Assignment	RS name	Formula
RS01	EP1 mL	'Molarity NaOH with HCl.EP{1}.VOL'
RS02	Slope	'RS.EP1 mL.SLO'
RS03	Intercept	'RS.EP1 mL.ITC'
RS04	Correlation	'RS.EP1 mL.COR' * 'RS.EP1 mL.COR'
RS05	Molarity	'Standard HCl.CONC'/'RS.EP1 mL.SLO
RS06	mmol HCl	'MV.Sample size' * Standard HCl.CONC'

Molarity $Al(NO_3)_3$

Assignment	RS name	Formula
RS01	EP1 mL	'Molarity NaOH with HCl.EP{1}.VOL'
RS02	Slope	'RS.EP1 mL.SLO'
RS03	Intercept	'RS.EP1 mL.ITC'
RS04	Correlation	'RS.EP1 mL.COR' * 'RS.EP1 mL.COR'
RS05	Molarity	'RS.Slope' * 10/6
RS06	mmol KF	'MV.Sample size'

The molarity of $Al(NO_3)_3$ titrant is computed after titrating a range of volumes of standard NaF solution:

c($Al(NO_3)_3$) mol/L = slope*10/6, where the input sample size is mmol of standard NaF solution.

The value for the molarities of the standard solutions are stored in Configuration>Titrants/ Solutions>Concentration against the relevant Dosino.

The following methods are available to perform these determinations:

- Automated molarity of HCl
- Automated molarity of NaOH by standard HCl
- Automated Al titrant standardization for fluoride

Calculations for method blanks

The method blank is determined by titrating different amounts of a representative sample of the product and plotting the sample amount against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in titrant dose rate or filter factor will require a new determination of the method blank. While a change in the titrant dose rate will require a new set of titrations to be run, a change in the filter factor can be performed by editing the set of titration data stored in the database.

This parameter is stored along with the other method parameters. For all determinations, it is subtracted from the volume of titrant.

In the case of the three titrations comprising this determination, the method blanks were determined as follows:

- *NaOH titration of total acids*: from a range of volumes of a sample containing high concentrations of HNO_3, HF and H_2SiF_6

- *HCl back-titration of excess NaOH*: from the intercept computed as a result of the determination of the molarity of the NaOH

- *Al titration of HF content:* from the intercept computed as a result of the determination of the molarity of the $Al(NO_3)_3$ titrant.

Before performing a blank determination, it is important to set up Common Variables (CVs) for each of the respective method blanks under «Configuration». These CVs can be entered automatically during the blank determination titration run by double-clicking on the lines for "EP1 intercept" in each result table, selecting the "Options" tab, and checking the box "Save result as common variable", then selecting the correct CV title.

Calculation for method blank in tiamo^{TM}

Assignment	RS name	Formula
RS01	EP1 mL	'NaOH Titration.EP{1}.VOL'
RS02	Slope	'RS.EP1 mL.SLO
RS03	Intercept - blank	'RS.EP1 mL.ITC'
RS04	Corr Coeff	'RS.EP1 mL.COR' * 'RS.EP1 mL.COR'

The method *"Automated blank detn-NaOH titration HNO_3+HF+H_2SiF_6"* is available to perform this determination.

Calculations for HNO_3, HF and H_2SiF_6 determinations in tiamo^{TM}

Notes:

- These methods were set up with the assumption that in normal routine analysis, single determinations only would be required.
- Two procedures were developed for etch acid mixtures: one for freshly prepared etch mixtures containing HNO_3 and HF only and uncontaminated by H_2SiF_6, and one for "used" solutions where H_2SiF_6 is present.
- *"Fresh" HNO_3+HF solutions.* In this procedure, the total HNO_3+HF content is determined by NaOH titration. The titration is automatically stopped after the endpoint, and acetate buffer is added before titrating the F^- content with Al^{3+}.

Calculation of HF and HNO_3 content

Assignment	RS name	Formula
RS01	HNO_3+HF EP	'NaOH Titration HNO_3+HF.EP{1}.VOL'
RS	HF EP	'Al titration HF.EP{1}.VOL'
RS	HF g/L	(('RS.HF EP'- 'CV.Blank Total Etch Acids') * 'Al titration HF.CONC' * 6/'MV.Sample size'
RS	HNO_3 g/L	((('RS.HNO_3+HF EP'- 'CV.Blank Total Etch Acids')*'NaOH Titration HNO_3+HF.CONC'*63.01284)/'MV.Sample size')-('RS.HF g/L'*63.01284/20.00634)

The method "*Automated Fresh Etch Acid Mix HNO_3 HF* " is available for this procedure.

"Used" HNO_3+HF+H_2SiF_6 solutions

In this procedure, two separate, successive titration sequences are employed. In the first sequence, an aliquot is titrated first with c(NaOH)=2 mol/L for the total (HNO_3+HF+H_2SiF_6) content (expressed as HNO_3). The titration is allowed to proceed through the endpoint to a pre-set volume of NaOH. A second, back titration with c(HCl) = 2 mol/L titrates the excess of NaOH. This permits the calculation of the H_2SiF_6 content.

A titration with c($Al(NO_3)_3$) = 0.5 mol/L titrant on a second aliquot of sample for the HF content is then carried out immediately after the preceeding determination. This result is then subtracted from the residual (HNO_3+HF) result in the first determination to yield the HNO_3 result.

Calculations from NaOH-HCl titrations:

Individual calculations:

- *Calculation of total etch acids*
- *Calculation of adjusted titrant consumption due to H_2SiF_6 content*
- *Calculation of H_2SiF_6 content*
- *Calculation of residual HF + HNO_3 content*

Assignment	RS name	Formula
RS05	Total Etch Acids as HNO_3 g/L	(('NaOH Titration.EP{1].VOL'-'CV.Blank Total Etch Acids')*'NaOH Titration.CONC'*63.01284)/MV.Sample size'
RS06	Adjusted H_2SiF_6 titration vol	'NaOH Titration.EVT'-'NaOH Titration.EP{1}.VOL'-(('HCl back titration.EP{1}.VOL'-'CV.Blank HCl BT Etch Acids')*'HCl back titration.CONC'/'NaOH Titration.CONC'
RS07	H_2SiF_6 g/L	('RS.Adjusted H2SiF6 titration vol'*'NaOH Titration.CONC'*144.0918)/('MV.Sample size'*6)
RS08	HF+HNO_3g/L (as HNO_3)	'RS.Total Etch Acids as HNO_3 g/L'-('RS.H_2SiF_6 g/L'*2*63.01284/144.0918

Calculations from HF titration:

HF and HNO_3 content

Assignment	RS name	Formula
RS09	HF g/L	(('Al titration.EP{1}.VOL'-'CV.Blank HF by Al')*'Al titration.CONC'*20.00634*6)/('MV.Sample size')
RS10	HNO_3 g/L	'CV.HF+HNO_3 g/L'-('RS.HF g/L'*63.01284/20.00634)
RS11	H_2SiF_6 g/L	'CV.H_2SiF_6 g/L'

The methods "Automated Etch Acid Mix HNO_3-HF-H_2SiF_6 by NaOH-HCl " and "Automated HF in etch acid mixtures " are available for conduct of this procedure.

Methods

NOTE ON OPTIMAL SETUP OF TITRATION ASSEMBLY:
It is essential that the titration assembly be so adjusted, that the propeller stirrer is ~ 1 mm above the bottom of the titration tube at the fully lowered position. The Thermoprobe and the fluid delivery tubes should be 1 mm above the tips of the propeller. It is recommended that the fluid delivery tubes be tied together with a plastic tie about 35 mm from the bottom, and the group of delivery tips be angled towards the Thermoprobe. The direction of rotation of the stirrer must be set to carry the fluid delivered away from the sensor of the Thermoprobe to minimize noise. This setup should be used for all automated determinations.

Procedures for determination of titrant molarities

Determination of HCl molarity using TRIS

Use the method *"Automated molarity of HCl"*. Set up a 10 mL Dosino with c(HCl) = ~ 2 mol/L. Weigh accurately into separate titration tubes amounts of TRIS approximating 0.4, 0.6, 0.8, 1.0 and 1.2 g. Add 30 mL deion. water into each tube. *Note: more tubes may be prepared if desired, with masses of TRIS falling within the range 0.4-1.2 g*. Place in the sample rack of the 814 Sample Processor. Create a sample table with 5 positions, entering the above method and the mass of TRIS into each position.

Determination of NaOH molarity using standard c(HCl) = 2 mol/L

Use the method *"Automated molarity of NaOH by standard HCl "*. Set up a 20 mL Dosino with c(NaOH) = ~ 2 mol/L. Prepare 7 tubes containing deion. water as follows:

Tube no.	mL deion. water	c(HCl) = 2 mol/L to be dispensed, mL
1	28	2
2	27.5	2.5
3	27	3
4	26.5	3.5
5	26	4
6	25.5	4.5
7	25	5

Enter the volume of c(HCl) = 2 mol/L to be dispensed into the appropriate sample position in the sample table.

1.3 Determination of $Al(NO_3)_3$ molarity using standard NaF solution

Use the method *"Automated Al titrant standardization for fluoride"*. Prepare a solution of c(NaF) = 0.5 mol/L from freshly dried anhydrous A.R. NaF. Calculate the actual molarity from the accurately weighed mass of NaF. Prepare a series of titration tubes according to the table, using a bulb pipette to dispense the c(NaF) = 0.5 mol/L solution:

Tube no.	mL deion.water	mL c(NaF) = 0.5 mol/L
1	25	5
2	20	10
3	15	15
4	10	20
5	5	25
6	0	30

Calculate the actual mmol of NaF dispensed into each tube, and enter into the appropriate position in the sample table.

2. Procedure for method blank determination:

A method blank for the type of sample under examination is determined by titrating a range of sample amounts and calculating the y-intercept (in mL) of a regression curve, formed by plotting sample amount (x-axis) against mL of titrant delivery (y-axis). This can be done automatically in ***tiamo***™.

In the work reported here, it was considered necessary to only determine the blank value for the "total acids" titration with c(NaOH) = 2 mol/L, to account for any possible matrix effects.

For this determination, use the method *"Automated blank detn-NaOH titration $HNO_3+HF+H_2SiF_6$".*

Into 5 titration tubes, weigh accurately amounts of a suitable "used" etch acid mixture with a HNO_3 content in the range 550-600 g/L. The following table can be used as a guide:

Tube no.	mL deion. water	Sample mass, g
1	30	0.8
2	30	0.9
3	30	1
4	30	1.1
5	30	1.2

Enter the accurate masses of acid weighed into the sample table.

Procedure for analysis of acid mixtures

"Fresh" acid mixtures (no H_2SiF_6)

Use method "*Automated Fresh Etch Acid Mix HNO_3 HF ".*

Pipette a 1 mL sample into a titration tube, and dilute with 30 mL deion. water.

"Used" acid mixtures containing H_2SiF_6.

Use methods *"Automated Etch Acid Mix HNO_3-HF-H_2SiF_6 by NaOH-HCl "* and *"Automated HF in etch acid mixtures "*. Pipette 1 mL samples into each of two titration tubes. Dilute sample in the first tube with 30 mL deion. water and that in the second tube with 15 mL water. Place the first tube into position 1 of the sample rack (or an odd-numbered position) and the second tube into position 2 (or an even-numbered position). The difference in the amounts of dilution water is due to the addition of 15 mL of acetate buffer before the start of the determination of HF.

Prepare the sample table with the method *"Automated Etch Acid Mix HNO_3-HF-H_2SiF_6 by NaOH-HCl "* assigned to odd-numbered positions and method *"Automated HF in etch acid mixtures" to even-numbered positions.*

Results

Titrants:

Molarity of c(HCl) = 2 mol/L titrant

Slope	4.1
Intercept, mL	0.07
Correlation (R^2)	1.0000
Molarity [mol/L]	2.01
Titrant dose rate mL/min	4
Filter factor	40

Molarity of c(NaOH) = 2 mol/L

Slope	1.0100
Intercept, mL	0.0906
Correlation (R^2)	1.0000
Molarity [mol/L]	1.9940
Titrant dose rate mL/min	4
Filter factor	40

Blank determination "total acids"

Slope	4.9217
Intercept, mL	0.1111
Correlation (R^2)	1.0000
Titrant dose rate mL/min	4
Filter factor	40

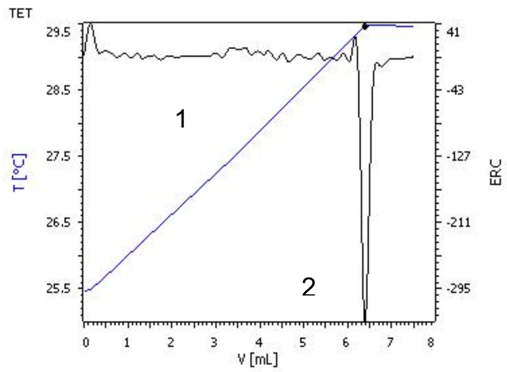
Synthetic etch acid mixtures

Sample no.	HNO_3 g/L	HF g/L	H_2SiF_6 g/L
1	323.5±0.59 (n=6)	158.3±0.15 (n=6)	-
2	404.4±0.52 (n=6)	123.1±0.23 (n=6)	-
3	410.7±0.89 (n=6)	104.1±0.16 (n=6)	11.1±0.16 (n=6)
4	410.1±0.92 (n=6)	69.1±0.26 (n=6)	47.9±0.23 (n=6)
5	598.8±0.41 (n=6)	54.0±0.14 (n=6)	73.6±0.15 (n=6)
6	200.6±0.52 (n=6)	44.4±0.05 (n=6)	185.2±0.36 (n=6)

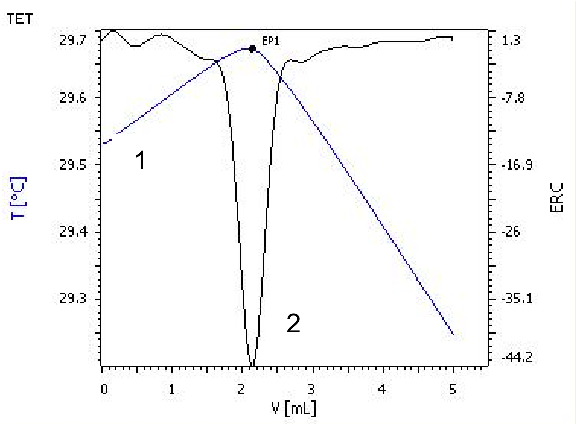
Titration plots:

"Fresh" HNO_3-HF mixture (sample 2)

"Total Acids" titration with c(NaOH) = 2 mol/ L

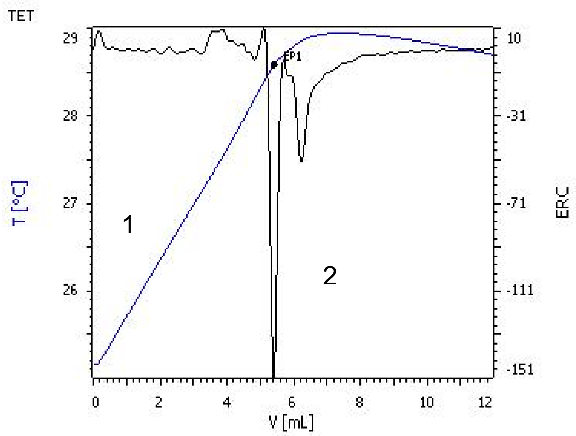


$c(Al(NO_3)_3)$ = 0.5 mol/L titration for HF content (linked to NaOH titration)

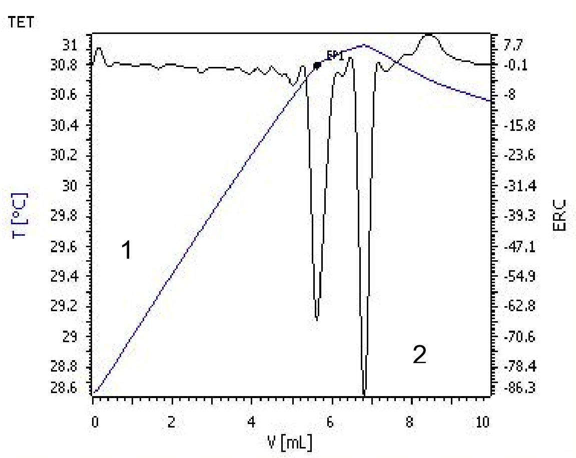


"Used" HNO_3-HF-H_2SiF_6 mixture (sample 4)

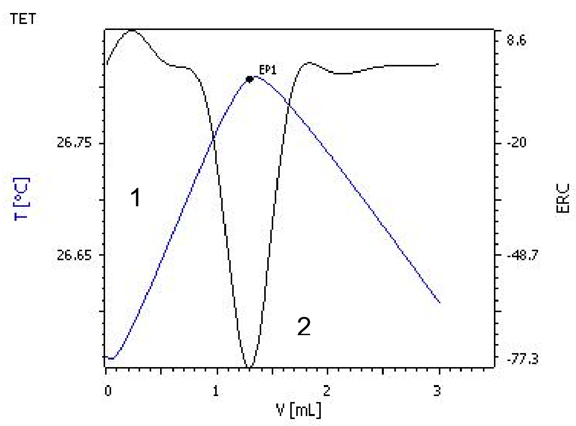
"Total Acids" titration with c(NaOH)=2 mol/L



c(HCl)=2 mol/L back-titration (linked to NaOH titration)

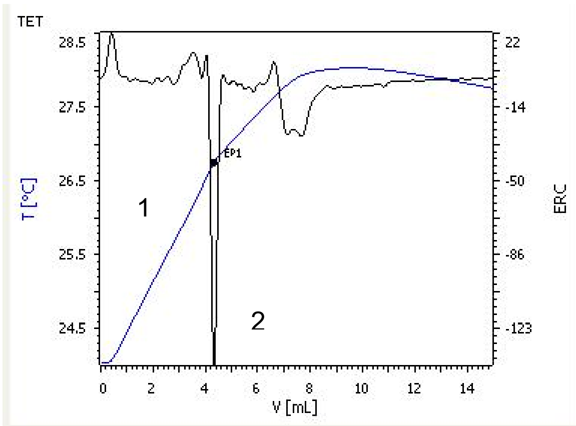


$c(Al(NO_3)_3)$=0.5 mol/L titration for HF content (separate titration, results linked to foregoing)

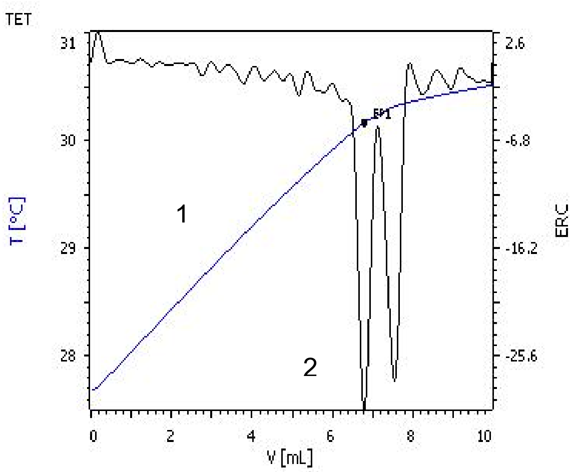


"Used" HNO_3-HF-H_2SiF_6 mixture with high H_2SiF_6 content (sample 6)

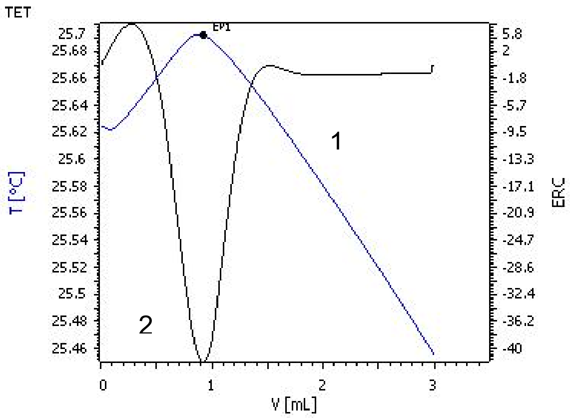
"Total Acids" titration with c(NaOH) = 2 mol/L



c(HCl) = 2 mol/L back-titration (linked to NaOH titration)



$c(Al(NO_3)_3)$ = 0.5 mol/L titration for HF content
(separate titration, results linked to foregoing)



Notes:

1 = solution temperature
2 = second derivative curve (for endpoints)
EP1 = selected endpoint for computation.

Notes on safe usage and disposal of ammonium bifluoride, $NH_4F.HF$.

$NH_4F.HF$ and its solutions are toxic and corrosive. It is highly recommended that this reagent is added automatically using a Dosino with an ETFE burette as part of the titration method program to minimize the chance of possible contact. The reagent should be stored and dispensed from a polypropylene or polyethylene container.

Wear appropriate protective clothing, including disposable rubber gloves and safety glasses with sideshields. Adhere to recommendations in MSDS documentation.

All staff required to handle this reagent should be trained in its use and regularly monitored to ensure adherance to safe working practices.

Disposal of $NH_4F.HF$ solutions and residues containing $NH_4F.HF$ should be in accordance with local regulations. Solutions containing fluoride ion may be treated by reacting with an excess of boric acid, H_3BO_3.