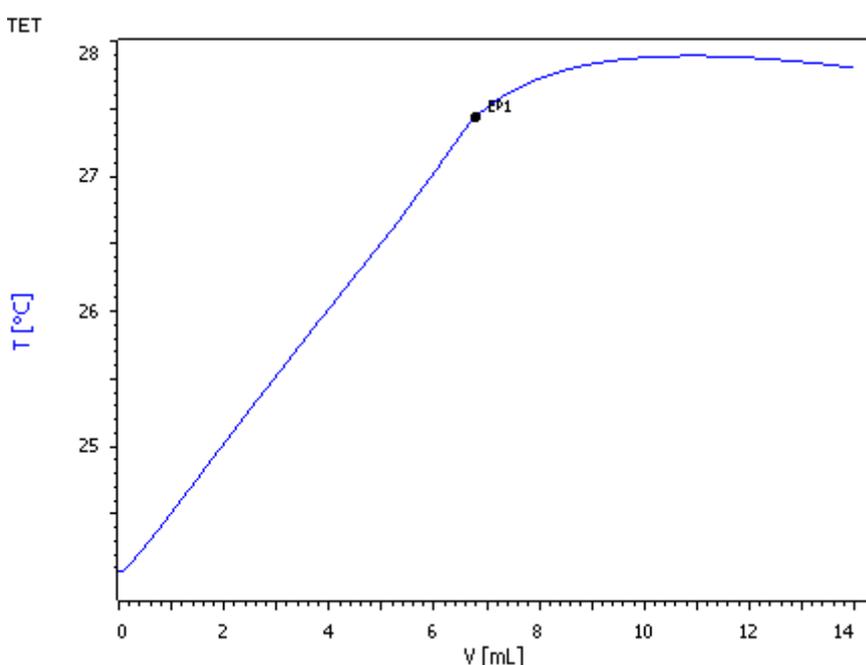


Determination of nitric, hydrofluoric, and hexafluorosilicic acid in etching baths by thermometric titration



After addition of NaOH, hexafluorosilicic acid can be determined by back-titrating the NaOH excess with hydrochloric acid. Hydrofluoric acid can be determined by precipitation with aluminum in presence of sodium and potassium ions. Nitric acid can be determined by subtracting the equivalence concentration of hexafluorosilicic and hydrofluoric acid from the total acid concentration.

Method description

Sample

Synthetic etch-bath solution

Sample preparation

No sample preparation is required

Configuration

859 Titrotherm	2.859.1010
846 Dosing Interface	2.846.0010
804 Ti Stand	2.804.0010
800 Dosino, 5x	2.800.0010
20 mL Dosing Unit, 3x	6.3032.220
50 mL Dosing Unit	6.3032.250
5 mL Dosing Unit ETFE	6.1575.150
Thermoprobe HF	6.9011.040

Solutions

Titrant 1	$c(\text{NaOH}) = 2 \text{ mol/L}$ 80 g sodium hydroxide is weighed into a 1000 mL volumetric flask and filled up to the mark with deionized water
Titrant 2	$c(\text{HCl}) = 2 \text{ mol/L}$ 227.69 g concentrated hydrochloric acid is weighed into a 1000 mL volumetric flask and filled up to the mark with deionized water.
Titrant 3	$c(\text{Al}(\text{NO}_3)_3) = 0.5 \text{ mol/L}$ 187.6 g aluminum nitrate nonahydrate is weighed into a 1000 mL volumetric flask and filled up to the mark with deionized water
Solvent	Acetate buffer at pH 4.5 1.11 mol (91.05 g) anhydrous sodium acetate and 0.5 mol (49.07 g) potassium acetate are weighed into a 1000 mL volumetric flask. 100 mL glacial acetic acid is added and the flask is filled up to the mark with deionized water.

Analysis

Blank total acid and hexafluorosilicic acid determination

A linear regression of different sample sizes against consumption is performed. 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL sample solution respectively is pipetted into a titration beaker and 30 mL deionized water is added. The solution is titrated with $c(\text{NaOH}) = 2 \text{ mol/L}$ to one exothermic endpoint (total acid content). Afterwards 7 mL sodium hydroxide $c(\text{NaOH}) = 2 \text{ mol/L}$ is added to give an excess of hydroxide ions. The solution is then back-titrated with $c(\text{HCl}) = 2 \text{ mol/L}$ until the second exothermic endpoint (rebuilding the hexafluorosilicic anion).

Blank hydrofluoric acid determination

A linear regression of different sample sizes against consumption is performed. 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL sample solution is pipetted into a titration beaker and 35 mL solvent is added, respectively. The solution is titrated with $c(\text{Al}(\text{NO}_3)_3) = 0.5 \text{ mol/L}$ until after the first exothermic endpoint.

Sample determination

The sample analysis is performed in the same way as the blank determination but without the linear regression.

Parameters

Blank total acid

Stirring rate	14
Dosing rate	6 mL/min
Filter factor	60
Damping until	0.5 mL
Stop slope	0.400 °C/mL
Stop slope active after	0.5 mL
Evaluation start	0.5 mL
EP criterion	-30
Reaction type	exothermic

Blank hexafluorosilicic acid

Stirring rate	14
Dosing rate	3 mL/min
Filter factor	45
Damping until	0.5 mL
Stop slope	-0.065 °C/mL

Method description

Stop slope active after	0.5 mL
Evaluation start	0.5 mL
EP criterion	-30
Reaction type	exothermic

Blank/Sample hydrofluoric acid

Stirring rate	14
Dosing rate	4 mL/min
Filter factor	45
Damping until	0.5 mL
Stop slope	Off
Stop slope active after	0.5 mL
Evaluation start	0.5 mL
EP criterion	-20
Reaction type	exothermic

Sample total acid

Stirring rate	14
Dosing rate	6 mL/min
Filter factor	60
Damping until	0.5
Stop slope	0.335 °C/mL
Stop slope active after	0.5 mL
Additional volume after stop	7 mL
Evaluation start	0.5 mL
EP criterion	-30
Reaction type	exothermic

Sample hexafluorosilicic acid

Stirring rate	14
Dosing rate	3 mL/min
Filter factor	45
Damping until	0.5
Stop slope	0.020 °C/mL
Stop slope active after	0.5 mL
Evaluation start	0.5 mL
EP criterion	-20
Reaction type	exothermic

Results

Acid contents (n = 5)

Sample	Recovery HNO ₃ / %	S(rel) / %
Etch-Bath 1	102.9	0.19
Etch-Bath 2	101.2	0.07
Etch-bath 2.1	97.5	0.27

Sample	Recovery HF / %	S(rel) / %
Etch-Bath 1	103.5	0.30
Etch-Bath 2	101.8	0.19
Etch-bath 2.1	105.2	0.55

Sample	Recovery H ₂ SiF ₆ / %	S(rel) / %
Etch-Bath 1	90.8	0.43
Etch-Bath 2	91.8	0.24
Etch-bath 2.1	91.93	0.39