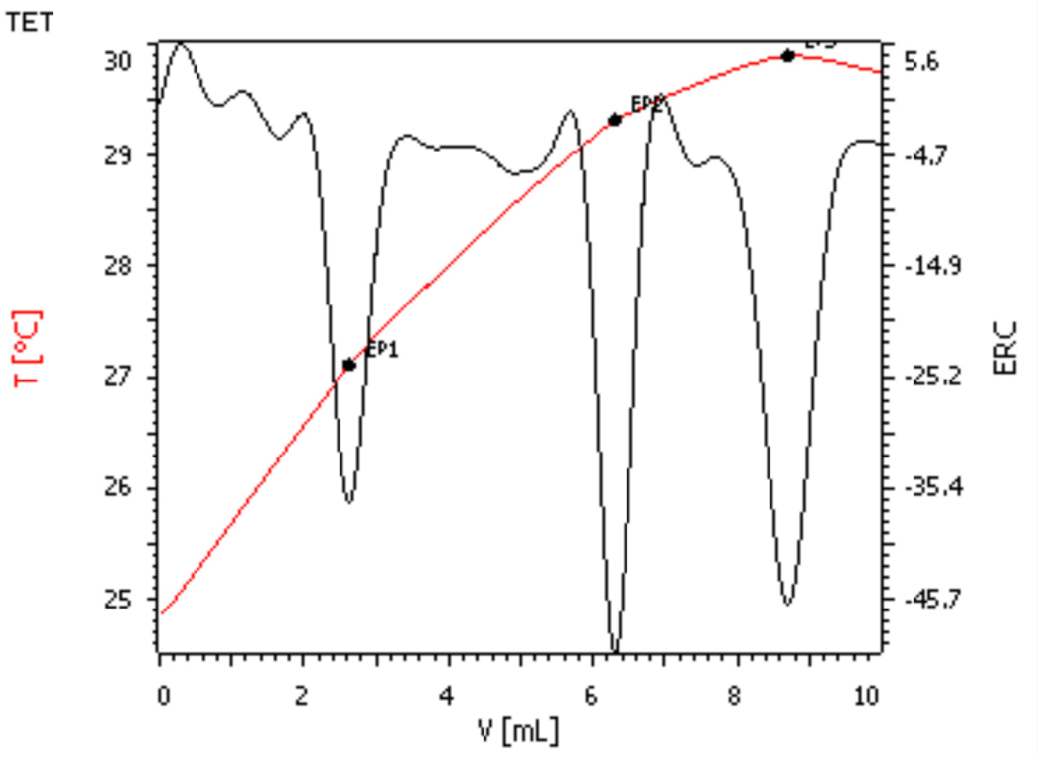
Titration Application Note H–16

Determination of acetic, phosphoric, and nitric acid mixtures



This Application Note looks at the determination of mixtures of phosphoric, nitric, and acetic acids used in etching of aluminum in the manufacture of semiconductor devices.

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Method description

Principle

Determination of mixtures of phosphoric, nitric, and acetic acids used in etching of aluminum in the manufacture of semi-conductor devices.

Titration with standard NaOH to obtain three endpoints

Endpoint 1	Endpoint 2	Endpoint 3
HNO_3 (fully dissociated)	CH_3COOH (pKa = 4.75)	
H_3PO_4 (pKa1 = 2.12)	H_3PO_4 (pKa2 = 7.21)	H_3PO_4 (pKa3 = 12.36)

Samples

Synthetic acid mixture:

H_3PO_4 [%]	HNO_3 [%]	CH_3COOH [%]
~61.0	~4.0	~21.0

Sample preparation

6.1217 g of acid mixture was weighed into a 200 mL volumetric flask, 120 mL saturated NaCl solution was added, and the flask made to volume with DI water. Aliquots of 25 mL ≡ 0.7652 g of sample were titrated.

Configuration

Basic equipment list for automated titration

814 USB Sample Processor	2.814.0030
859 Titrotherm	2.859.0010
Sample rack 24 x 75 mL	6.2041.340
Thermoprobe	6.9011.020
Sample beaker 75 mL	6.1459.400
802 Rod Stirrer	2.802.0010
Stirring propeller (104 mm)	6.1909.020
1 x 800 Dosino	2.800.0010
1 x Dosing unit 10 mL	6.3032.210
tiamo™	6.6056.222

Solutions

Titrant	2 mol/L NaOH
Solution	NaCl solution, saturated, approximately 35% w/v
Standard substance	potassium hydrogen phthalate, dried 2 hours at 110 °C
Stirring speed (802 Rod Stirrer)	15

Analysis

Approximately 10 mL deionized water and 15 mL saturated NaCl solution is dispensed into a titration vessel. The vessel is then tared or weighed on a balance reading to 0.1 mg. Approximately 0.5 mL of concentrated acid mixture is then rapidly dispensed into the vessel and then re-weighed. The mass of dispensed acid is entered into the software. For assays of dilute solutions, an aliquot up to 10 mL can replace all or part of the deionized water content of the beaker. Alternatively, approximately 4 mL of concentrated acid mixture is weighed directly into a 200 mL volumetric flask. 120 mL saturated NaCl solution is added, and the contents made to volume with deionized water. 25 mL aliquots are taken for titration. The solution is titrated with standardized 2 mol/L NaOH to obtain 3 exothermic endpoints.

Titrant standardization c(NaOH) = 2 mol/L

Weigh accurately into clean, dry titration tubes amounts of approximately 0.4, 0.8, 1.2, 1.6, 2.0, and 2.4 g freshly dried potassium hydrogen phthalate. Add to each 25 mL DI water, and place in rack of 814 Sample Processor. Perform standardization titration. The method automatically computes titrant molarity and the correlation coefficient.

Determination of systematic errors („blanks")

Because results are dependent on the differences in endpoint values, it is important to ascertain any errors in determining these differences, which are essentially systematic errors. These errors are subtracted from the differences in endpoint volumes when computing the results.

Into clean, dry titration vessels, weigh accurately amounts of a typical acid mixture sample of approximately 0.2, 0.4, 0.6, 0.8, and 1.0 g. To each vessel, add 15 mL of saturated NaCl solution and 10 mL of DI water and titrate.

Perform 3 separate regression analyses, plotting **EP1**, **EP2-EP1** and **EP3-EP2** on the y-axis against sample mass in g on the x-axis (see following plots). Store these blank values as Common Variables (CV's).

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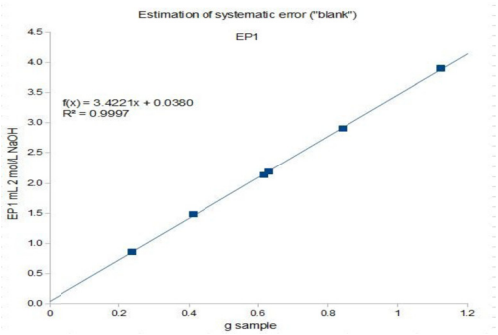
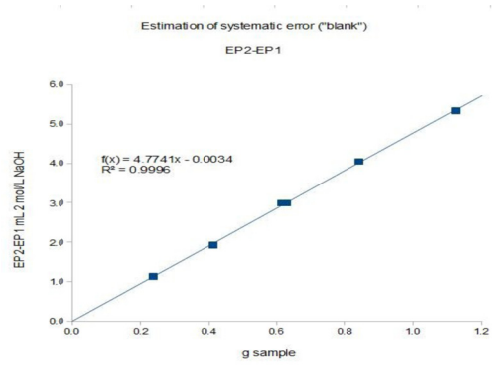
Method description

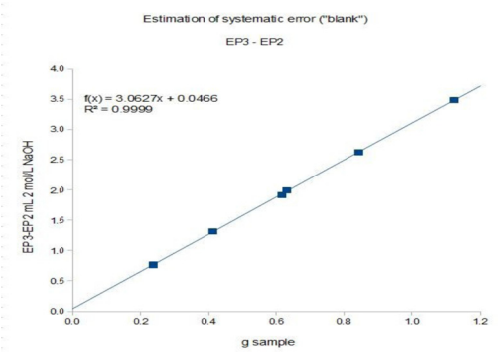
Results of blank determinations



Blank determination EP1 = 0.0380 mL



Blank determination EP2 - EP1 = - 0.0034 mL



Blank determination EP3 - EP2 = 0.0466 mL

Parameters

Titrant dose rate	2 mL/min
No. of exothermic endpoints	3
Data smooting (“filter factor”)	65
Stirring speed (802 Rod Stirrer)	15

Calculations

% H_3PO_4 = (EP3 - EP2 - blank EP3 - EP2) × C01 × C02 × 0.1)/C00

% HNO_3 = ((EP1 - blank EP1 - (EP3 - EP2) - blank EP3 - EP2)) x C01 x C03 x 0.1)/C00

% CH_3COOH = ((EP2 - EP1 - blank EP2 - EP1 - (EP3 - EP2 - blank EP3 - EP2)) × C01 × C04 × 0.1)/C00

EP1 = endpoint in mL
EP2 = endpoint in mL
EP3 = endpoint in mL
C00 = sample weight in g
C01 = concentration of titrant in mol/L
C02 = molecular weight of H_3PO_4 (97.99518 g/mol)
C03 = molecular weight of HNO_3 (63.01284 g/mol)
C04 = molecular weight of CH_3COOH (60.05196 g/mol)
0.1 = conversion factor to %

Results and discussion (mean and standard deviation values)

H_3PO_4 [%]	HNO_3 [%]	CH_3COOH [%]
61.4	4.0	21.6
61.6	4.0	21.3
61.4	3.9	21.9
62.0	4.2	20.9
61.2	4.4	21.7
61.8	4.0	21.2
61.6	4.2	21.4
61.6 ± 0.3	**4.1 ± 0.2**	**21.4 ± 0.3**

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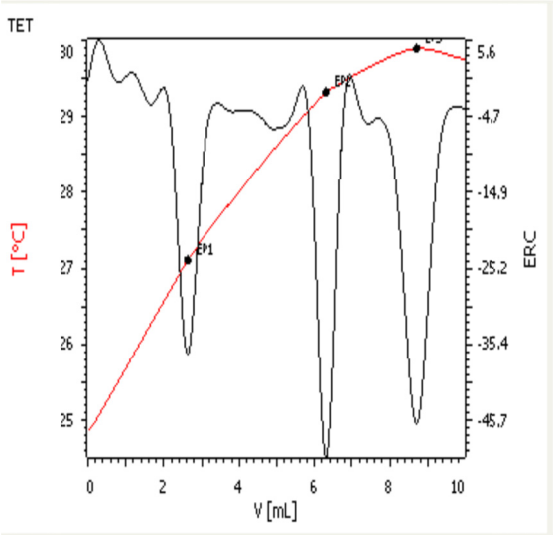
Titration plots



Thermometric titration plot of a mixture of H_3PO_4, HNO_3, and CH_3COOH with 2 mol/L NaOH.

Legend
Red curve: temperature of the solution
Black curve: second derivative of solution temperature (ERC = «endpoint recognition criterion»; in this case, the second derivative)

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