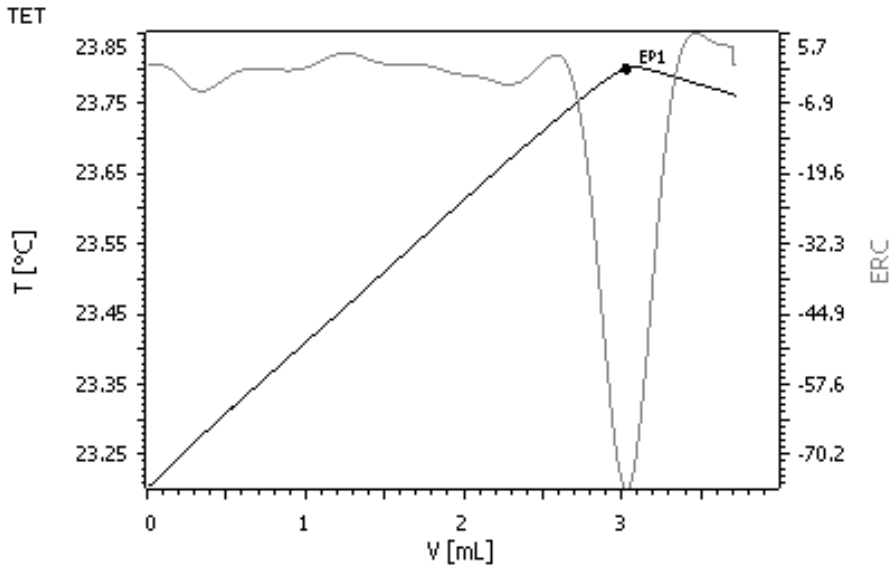
Titration Application Note H–116

Determination of sulfate in phosphoric acid by standard addition of sulfuric acid



This Application Note augments AN-H-003 by considering the standard addition of sulfate as sulfuric acid. This technique may be contemplated when either sulfate levels are too low for a satisfactory direct titration, or when the sample matrix causes excessive rounding of the endpoint inflection, leading to poor precision and accuracy.

Metrohm

Method description

Principle

Barium ion reacts exothermically with sulfate ion to form insoluble barium sulfate, providing the basis for a thermometric titration. In many industrial solutions, other ions present may interfere with the reaction, leading to rounded endpoint inflections with inaccurate and/or imprecise results. The levels of sulfate present may also vary considerably, and the direct titration of sulfate can be challenging at levels at or below approximately 0.2% or 2 g/kg.

Both of these problems may be overcome by the addition of a set amount of a sulfate solution, to boost the amount of sulfate present by a considerable amount. It has been found that the thermometric titration of sulfate proceeds optimally in strongly acidic solutions, so sulfate is added in the form of sulfuric acid, accompanied by hydrochloric acid. A mixed solution of 0.1 mol/L H_2SO_4 and 0.5 mol/L HCl is used for this purpose. This solution strength is suitable for safe use by semi-skilled operators.

Samples

Sample preparation

Samples analyzed comprised two samples of impure industrial-grade phosphoric acid («reactor acid»), and two samples of more dilute samples from a pilot plant trialing a new process with an unknown ore type

Configuration

Basic equipment list for automated titration

814 USB Sample Processor	2.814.0030
859 Titrotherm	2.859.0010
Sample rack 24 × 75 mL	6.2041.340
Thermoprobe HF resistant*	6.9011.040
Sample beaker 75 mL	6.1459.400
802 Rod Stirrer	2.802.0010
Stirring propeller 104 mm	6.1909.020
2 × 800 Dosino	2.800.0010
1 × Dosing unit 50 mL	6.3032.250
1 × Dosing unit 5 mL	6.3032.150
tiamo™	6.6056.222

** HF is a common impurity in industrial phosphoric acid, due to the presence of fluorapatite in apatite ores.*

Solutions

Titrant	$c(BaCl_2)$ = 1 mol/L barium chloride solution (standardized)
	$c(H_2SO_4)$ = ~0.1 mol/L H_2SO_4 in c(HCl) =~0.5 mol/L *This solution does not require prior standardization*

Initial determination of reagent blank

A 25 mL aliquot of H_2SO_4/HCl solution is dispensed into a titration vessel, and the volume brought to ~30 mL with DI water. Preferably, this solution should be dispensed by Dosino as part of a *tiamo*™ titration program, although a 25 mL volumetric pipette may be used if the operator has sufficient analytical skill. The solution is titrated to an exothermic endpoint with standard $c(BaCl_2)$ = 1 mol/L, and the consumption of titrant noted. The mean of at least three determinations should be taken, with the maximum spread of results not exceeding 0.01 mL. The mean value should be stored in *tiamo*™ as a Common Variable (CV). Automated *tiamo*™ programs are available for determination of the reagent blank.

The reagent blank is constant for the same batches of $c(BaCl_2)$ = 1 mol/L and $c(H_2SO_4)$ = ~0.1 mol/L H_2SO_4 in c(HCl) =~0.5 mol/L. If new batches of either reagent are introduced, the reagent blank must be redetermined.

Analysis of samples

A sample of acid is weighed directly into a titration vessel. The amount of sample may vary from approximately 1 to 10 g, depending on the anticipated sulfate concentration (expressed as SO_4). It is recommended that the titration volume of $c(BaCl_2)$ = 1 mol/L should not exceed ~1.5 mL, after subtraction of the reagent blank.

Prior to titration, a 25 mL aliquot of H_2SO_4/HCl solution is dispensed into the vessel, either as part of the titration program or by volumetric pipette. The solution is then titrated to an exothermic endpoint with standard $c(BaCl_2)$ = 1 mol/L.

Metrohm

Method description

Parameters

Basic experimental parameters

Titrant dose rate (mL/min)	2
ERC EP1 (exothermic)	–25
Data smoothing («filter factor»)	50
Stirring speed (802 Rod Stirrer)	15
Evaluation start (mL)	0.5
Damping until (mL)	0.5

Calculations

$\%\ SO_4\ (w/w) = ((EP1 - blank) \times C001 \times C002 \times 0.1)/C00$

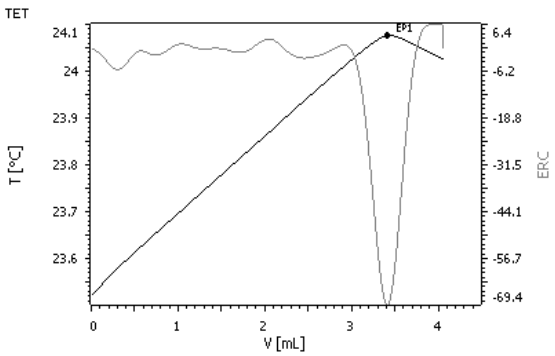
EP1 = endpoint in mL
blank = reagent blank of 25 mL of $c(H_2SO_4)$ =~0.1 mol/L
C00 = sample mass in g
C001 = concentration of titrant in mol/L
C002 = formula mass of SO_4 (96.0636 g/mol)

Results

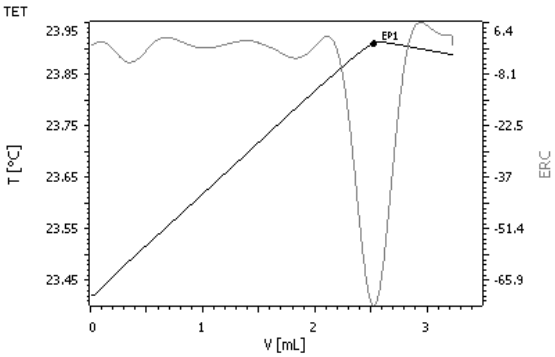
SO_4 in % (w/w)	
Reactor acid no.1	2.45 ± 0.014 (n=6)
Reactor acid no. 2	3.54 ± 0.021 (n=6)
Pilot plant sample no.1	0.20 ± 0.002 (n=6)
Pilot plant sample no. 2	1.14 ± 0.003 (n=6)

A fully automated determination is normally complete in < 3 min, including rinsing of the titration assembly between determinations.

Titration Plots



Titration of reactor acid no. 2 (SO_4 = 3.54% (w/w))



Titration of pilot plant sample no.1 (SO_4 = 0.20% (w/w))