Determination of sulfate in granular phosphate fertilizers with 859 Titrotherm

Of interest to: Fertilizer industry

Summary

Sulfate may be rapidly and easily titrated thermometrically using a standard solution of Ba^{2+} as titrant. Industrially, the procedure has been applied to the determination of sulfate in wet process phosphoric acid, where it has proven to be quite popular. This bulletin deals with the determination of sulfate in granular fertilizers such as MAP (mono-ammonium phosphate), DAP (di-ammonium phosphate) and TSP (triple superphosphate). Results are reported as percentage of elemental sulfure, %S.

Introduction

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.

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 10 mL Dosing unit included)
2 x 2.800.0010 800 Dosino
1 x 6.3032.210 Dosing unit 10 mL
1 x 6.3032.250 Dosing unit 50 mL
1 x 6.1543.210 3-way stopper with antidiffusion tip
1 x 6.1446.000 3 x SGJ stoppers
1 x 6.2061.010 Reagent organizer
1 x 6.2026.010 Support rod with stand
1 x 6.2065.000 Stacking frame

Reagents

Solvent: deionized water
Diluent: c(HCl) = 0.1 mol/L
Standard: Na_2SO_4 p.a.
Reaction solution: conc. HCl
Titrant: $c(BaCl_2)$ = 1 mol/L

Samples

From Company "A"
MAP 1-A
MAP 2-A
DAP 1-A

From Company "B"
MAP 1-B
MAP 2-B
TSP 1-B

Calculations

Titer $BaCl_2$ with Na_2SO_4

If a liquid primary standard is used, dose aliquots directly into the titration vessel. Set up an regression plot with the sample size on the x-axis and mL of titrant consumed on the y-axis. The plot will be a linear curve of the form y = a * x + b, where the molarity of the titrant is calculated from the slope (a) with the following formula: $(slope)^{-1}$ * c(standard solution)

Reaction: $Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

Calculation of titer in *tiamo*™

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept	'RS.EP.ITC'
RS04	Correlation (R^2)	'RS.EP.COR*'RS.EP.COR'
RS05	Molarity [mol/L] of titrant	(1/'RS.EP.SLO')*'Na_2SO_4'.CONC'
RS06	Titer of titrant	(1/,RS.EP.SLO')*'Na_2SO_4'.CONC'/ 'TET1.CONC'
RS07	Filter factor	'MV.filter factor'

Method blank

The method blank is determined by titrating a number of analyte solutions of different concentrations and plotting the analyte concentration against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in method parameters will require a new determination of method blank.
This parameter is stored along with the other method parameters. For all determinations it is subtracted from the volume of titrant.

Calculation of method blank in *tiamo*™

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept [mL]	'RS.EP.ITC'
RS04	Correlation (R^2)	'RS.EP.COR*'RS.EP.COR'
RS07	Filter factor	'MV.filter factor'

Calculation of sulfate determination in *tiamo*™

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS07	filter factor	'MV.filter factor'
RS08	%S	('TET1.EP(1).VOL'-'CV.blank')* 'TET1.CONC'*TET1.TITER'* 'MV.S'*0.1/'MV.sample size
RS09	Blank [mL]	'CV.blank'

Legend formula

'TET1.EP(1).VOL'	= Thermometric titration endpoint volume
RS	= result
EP	= endpoint
'RS.EP.SLO'	= slope for linear regression
'RS.EP.ITC'	= Intercept for linear regression
'RS.EP.COR*'RS.EP.COR'	= correlation coefficient (R^2)
'MV.filter factor'	= Titration parameter (smoothing factor)
CV.blank'	= method blank in mL
'Na_2SO_4'.CONC'	= concentration of standard Solution (0.5 mol/L)
'TET1.CONC'	= Concentration of the titrant (1 mol/L)
'TET1.TITER'	= titer of the titrant
'MV.sample size'	= sample size in g
'MW.Na_2SO_4'	= 142.04 g/mol
'MW.S'	= 32.065 g/mol
0.1	= factor for conversion in %

Method

Procedure for titer determination:

Dry anhydrous A.R. Na_2SO_4 for 2 hours at 200°C. Cool in a dessicator.
If a 10 mL Dosino is available for the purpose, a 0.5 mol/L Na_2SO_4 solution can be made up and a program set up to automatically dispense aliquots in the range 2 – 9 mL (1 – 4.5 mmol SO_4^{2-}). Pipette or dose up to 30 mL 0.1 mol/L HCl and start the titration.
The results are being additionally regressed against the sample size. In this application the molarity of the titrant $BaCl_2$ represents the titer which is automatically saved.The titer will be calculated automatically with the formula "Calculation of titer ***tiamo***™".

Procedure for method blank determination:

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

Weigh accurately a range of sample masses, from approximately 1 to 5 g directly into the titration vessels. Add 1 mL conc. HCl for each g of sample, and heat on a moderate hot plate until all sample has dissolved. Cool on a water bath.
Add 30 mL deionized water and titrate to a single thermometric endpoint.
The method blank is automatically calculated with the formula "Calculation of method blank ***tiamo***™". The intercept in mL, which represents the method blank, will be saved as a common variable. This blank has to be subtracted from each further analyzed sample.

Titration Parameters

	Titer determination	Blank determination	Samples
Stirring rate	10	10	10
Start volume [mL]	0	0.1	0.1
Pause [s]	20	60	120
Switch off autom.	yes	yes	yes
Dosing rate [mL/min]	6	6	6
Filter factor	30	40	40
Damping until [mL]	0.5	0.5	0.8
Stop volume [mL]	5.0	3.5	4.0
Stop slope	<0.06	off	off
Add. volume after stop [mL]	0.7	off	off
Evaluation start [mL]	0.5	0.5	0.5
End points [Reaction type]	ex*	ex*	ex*
EP criterion [ERC]	-40	-20	-12

* exothermic

Sample preparation for titer, blank and sample

	Titer determination	Blank determination	Sample determination
0.5 mol/L Na_2SO_4 [mL]	2 - 9	-	-
0.1 mol/L HCl diluent for standardization [mL]	to 30	-	-
Solvent (conc. HCl) [mL]	-	1 mL/g MAP sample	1 mL/g MAP sample 5 mL/3 g DAP sample
Diluent (deionized water) [mL]	-	30	to 30
Sample size in gram (fertilizer)	-	MAP 2-B = 1 - 5	MAP A = 3 MAP B = 4 DAP A = 3 TSP = 3
Number of determination (n =)	3 - 5	3 - 5	3 - 5

Procedure for sample preparation

1. MAP samples. Weigh accurately approximately 3 g sample directly into the titration vessel. Add 3 mL conc. HCl, and place on moderately heated hot plate. Equip vessel with a short stem funnel to act as splash trap. Heat until the sample is dissolved. Wash funnel with minimum deionized water and cool on a water bath. Make volume to 30 mL with deionized water and titrate with standard 1 mol/L $BaCl_2$ to a single thermometric endpoint.

2. DAP samples. Weigh accurately approximately 3 g sample directly into the titration vessel. Add 5 mL conc. HCl and process as for MAP samples.

3. TSP samples. Weigh accurately approximately 3 g of sample, and treat with 3 mL conc. HCl and 1 mL deionized water. Heat to a gentle boil and hold for 5 minutes. Treat sample as for MAP and DAP.
The sulfate content of the sample in % S is automatically calculated with the formula "Calculation of sulfate determination ***tiamo***™".

Note: Adjust sample mass to give an endpoint volume of ~2 mL in the case of MAP and DAP and ~1 mL in the case of TSP.

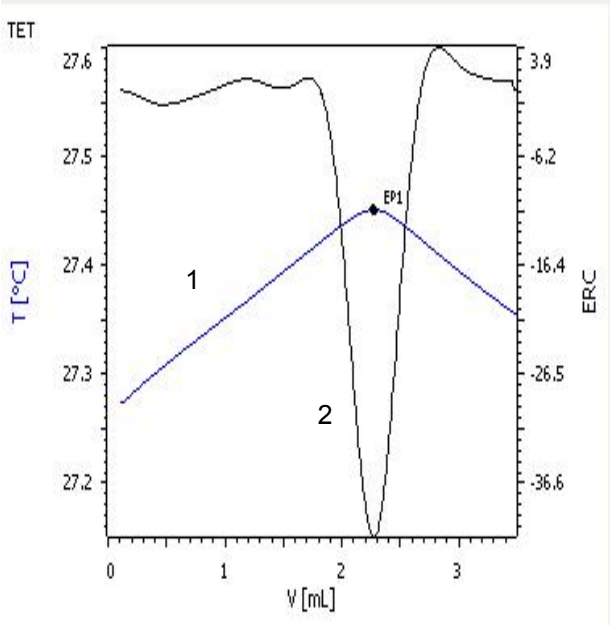
Results (titer and blank)

	Titer $BaCl_2$	Blank (on MAP 2-B)
Slope	0.4611	-
Intercept [mL]	0.1159	0.1465
Correlation (R^2)	1.0000	1.0000
Molarity [mol/L]	1.0852	-
Filter factor	30	40
Titer	1.0852	-

Results

Sample designation	% S
MAP 1-A	2.45, 2.45, 2.45 mean = 2.45
MAP 2-A	2.19, 2.19, 2.18 mean = 2.19
DAP 1-A	2.45, 2.46, 2.45 mean = 2.45
MAP 1-B	1.45, 1.46, 1.46 mean = 1.46
MAP 2-B	1.66, 1.66, 1.66 mean = 1.66
TSP 1-B	1.06, 1.07, 1.07 mean = 1.07

Thermometric Titration Plot (MAP 1-A)



Legend:

1 = solution temperature curve

2 = second derivative curve (for endpoints)