Determination of sulfate in phosphoric acid (liquid fertilizer samples) with 859 Titrotherm

Of interest to: fertilizer industry

Summary

Sulfate may be rapidly and easily titrated thermometrically using 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.

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 x 10 mL Dosing unit included)
2 x 2.800.0010	800 Dosino
1 x 6.3032.150	Dosing unit 5 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 6.2065.000	Stacking frame

Reagents

Solvent:	deionized water
Standard:	Na_2SO_4 p.a.
Reaction solution:	$c(HNO_3)$ = 5 mol/L
Titrant:	$c(BaCl_2)$ = 1 mol/L

Samples

Sample 1 and sample 2 are liquid phosphoric acid fertilizers from a customer

Calculations

Titer $BaCl_2$ titrant

If a solid primary standard is used, weigh it directly in the titration vessel. Set up an regression plot with the sample size on the x-axis and milliliters of titrant consumed on the y-axis. The plot will be a linear curve of the form y = a * x + b. The method automatically performs a regression analysis, computing the slope of the line of best fit, and from that, the molarity of titrant. Effectively, the program plots mL of titrant consumed against g of standard.

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

Calculation of titer in *tiamo*™

Assignment	RS name	formula
RS01	EP	'TET.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]	1/'RS.EP.SLO'*1000/142.04214
RS06	Titer	'RS.molarity/'TET.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 substracted from the volume of titrant.

Calculation of method blank in *tiamo*™

Assignment	RS name	formula
RS01	EP	'TET.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept	'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	'TET.EP(1).VOL'
RS07	Filter factor	'MV.filter factor'
RS08	$\%SO_4$	('TET.EP(1).VOL'-'CV.blank')*'TET.CONC'*TET.TITER'*96.0626*0.1/'MV.sample size
RS09	blank	'CV.blank'

Legend formula

'TET.EP(1).VOL'	= Thermometric titration endpoint Volume
RS	= Result
SLO	= Slope for linear regression
ITC	= Intercept for linear regression
COR	= Correlation coefficient (R^2) '
'MV.filter factor'	= Titration parameter (smoothing factor)
CONC	= Concentration of the titrant (1 mol/L)
CV	= Common variable
'CV.blank'	= Method blank in mL
Titer	= Titer of the titrant
MV	= Method variable
'MV.sample size'	= Sample size in g
MW	= Molar weight of the analyte
'MW.Na_2SO_4'	= 142.04214 g/mol
'MW.SO_4'	= 96.0626 g/mol
1000	= Conversion factor for liter
0.1	= Factor for conversion in %

Method

Procedure of titer determination:

Dry anhydrous A.R. Na_2SO_4 for 2 hours at 200°C. Cool in a dessicator. Weigh accurately 3 - 5 amounts ranging from approximately 0.1 – 0.6 g in roughly equal increments directly into the titration vessel. Add 1 mL of 5 mol/L HNO_3 with a pipette and 30 mL deionized water and start the titration. The titer will be calculated automatically with the formula "Calculation of titer ***tiamo***™". 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.

Procedure of 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 aliquote size (x-axis) against mL of titrant delivery (y-axis). This will be done automatically in ***tiamo***™.
Pipette approx. 5 – 7 gram of liquid fertilizer (no sample preparation necessary) directly into the titration vessel, 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	Liquid fertilizer
Stirring rate	6	8	8
Start volume [mL]	0	0.1	0
Pause [s]	10	20	20
Switch off autom.	yes	yes	yes
Dosing rate [mL/min]	6	7	7
Filter factor	60	50	50
Damping until [mL]	0.5	0.5	0.5
Stop volume [mL]	5.0	5.0	3.0
Stop slope	off	off	off
Add. volume after stop [mL]	off	off	0.5
Evaluation start [mL]	0.5	0.5	0.5
End points [Reaction type]	ex*	ex*	ex*
EP criterion [ERC]	-20	-20	-20

* exothermic

Sample preparation of titer, blank and sample

	Titer determination	Blank determination	Sample determination
Na_2SO_4 [g]	0.1 - 0.6	-	-
5 mol/L [mL]	1.0	-	-
Solvent (distilled water in mL)	30	30	30
Sample size in gram (fertilizer)	-	5 - 7	6
Number of determination (n =)	3 - 5	3 - 5	3 - 5

Procedure of sample preparation

Pipette approx. 6 gram of liquid fertilizer (no sample preparation necessary) directly into the titration vessel. Dose automatically 30 mL deionized water and titrate with standardized 1 mol/L $BaCl_2$ to a single thermometric endpoint. The sulfate content of the sample in $\%SO_4$ is automatically calculated with the formula "Calculation of sulfate determination ***tiamo***™".

Results (titer and blank)

	Titer $BaCl_2$	Blank sample 1	Blank sample 2
Endpoint [mL]	1.1600	1.9317	1.4583
Slope	7.0272	0.2486	0.1942
Intercept	0.0956	0.0274	0.0447
Correlation (R^2)	0.9996	0.9984	0.9999
Molarity [mol/L]	1.0019	-	-
Filter factor	60	50	50
Titer	1.0019	-	-

Results (phoshoric acid samples)

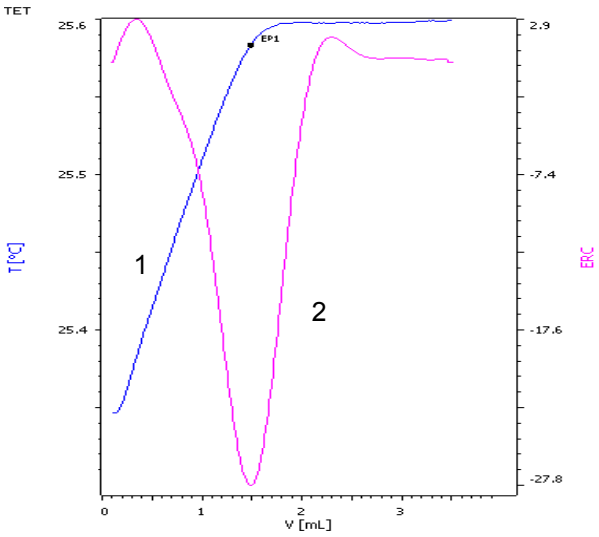
	sample 1	**sample 2**
$\%SO_4$	2.38; 2.40; 2.43	1.87; 1.84; 1.85
s(abs) $\%SO_4$	0.03	0.02
s(rel) %	1.04	0.86
n =	3	3

Expected values (customer information):

sample 1 = 2.15 - 2.45% SO_4

sample 2 = 1.53 - 1.83% SO_4

Thermometric Titration Plot (sample 1)



Legend:

1 = solution temperature curve

2 = second derivative curve (for endpoints)