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Determination of phosphoric acid in liquid fertilizer with thermometric titration

Of interest to: fertilizer industry

Summary

The phosphoric acid content may be easily titrated with a standardized solution of 2 mol/L NaOH. The disturbing calcium content in phosphoric fertilizer can be eliminated with the addition of saturated oxalate solution.

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:	Potassium hydrogen phthalate (PHP)
Conditioning solutions:	300 g/L NaCl
	300 g/L Potassium oxalate monohydrate $(C_2K_2O_4 \cdot H_2O)$
Titrant:	c(NaOH) = 2 mol/L

Samples

The analyzed sample is a liquid phosphoric acid fertilizer from a customer.

Calculations

Titer NaOH titrant

Weigh 3-5 amounts of PHP ranging from approximately 0.6 to 1.1 g directly into titration vessels. Add 30 mL, deionized water to each, and titrate according to the NaOH standardization method. The method allows sufficient time for the dissolution of the PHP before commencing the titration. The method automatically performs a regression analysis, computing the slope of the line of best fit, and from that, the molarity of the titrant. Effectively, the program plots mL of titrant consumed against g of standard.

Reaction

$C_8H_5KO_4 + NaOH \rightarrow C_6H_4(COO\text{-}Na)(COO\text{-}K)$

Calculation of titer in *tiamo*™

Assignment	RS name	formula
RS01	EP1	'NaOH.EP{1}.VOL'
RS05	Slope	'RS.EP1.SLO'
RS07	Intercept	'RS.EP1.ITC'
RS09	Correlation (R^2)	'RS.EP1.COR'*'RS.EP1.COR'
RS11	Molarity [mol/L]	1/'RS.slope'*1000 / 204.22
RS12	Titer	'RS.molarity'/'NaOH.CONC'
RS13	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
RS02	EP2	'Blank fertilizer.EP{2}.VOL'
RS03	EP3	'Blank fertilizer.EP{3}.VOL'
RS04	Difference [mL]	'Blank fertilizer.EP{3}.VOL'-'Blank fertilizer.EP{2}.VOL'
RS06	Slope	'RS.difference mL.SLO'
RS08	Intercept [mL]	'RS.difference mL.ITC'
RS10	Correlation (R^2)	'RS.difference mL.COR'*'RS.difference mL.COR'
RS13	Filter factor	'MV.filter factor'

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Calculation of H₃PO₄ determination in *tiamo*™

Assignment	RS name	formula
RS02	EP2	'sample fertilizer.EP{2}.VOL'
RS03	EP3	'sample fertilizer.EP{3}.VOL'
RS04	Difference [mL]	'sample fertilizer.EP{3}.VOL' - 'sample fertilizer.EP{2}.VOL'
RS13	Filter factor	'MV.filter factor'
RS14	Blank [mL]	'CV.blank'
RS15	%H₃PO₄	('RS.difference mL' - 'CV.blank') * 'sample fertilizer.CONC' * 'sample fertilizer.TITER' * 97.99518 * 100/'MV.Sample size' / 1000
RS16	%P	('RS.difference mL' - 'CV.blank') * 'sample fertilizer.CONC' * 'sample fertilizer.TITER' * 30.9737 * 100 / 'MV.Sample size' / 1000
RS17	%P₂O₅	('RS.difference mL' - 'CV.blank') * 'sample fertilizer.CONC' * 'sample fertilizer.TITER' * 141.94452 * 100 / 'MV.Sample size' / 1000

pKₐ values of phosphoric acids

Endpoint 1	Endpoint 2	Endpoint 3
H₃PO₄ (pKₐ1 = 2.12)	H₃PO₄ (pKₐ2 = 7.21)	H₃PO₄(pKₐ3 = 12.36)

Legend formula

EP1	= Endpoint of NaOH standardization
EP2	= Second endpoint of phosphate determination
EP3	= Third endpoint of phosphate determination
Difference [mL]	= Difference between third and second thermometric endpoint
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 (2 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.PHP	= Potassiumhydrogenphthalat 204.22 g/mol
MW.H₃PO₄	= 97.977 g/mol
MW.P	= 30.9737 g/mol
MW.P₂O₅	= 141.94452 g/mol
100	= calculation factor for %
1000	= conversion factor for liter

Method

Procedure of titer determination

Dry Potassiumhydrogenphthalat for 2 hours at 105°C and cool in a dessicator. Weigh accurately 3 - 5 amounts ranging from approximately 0.6 – 1.1 g in roughly equal increments directly into the titration vessel. Add 30 mL deionized water, stir the sample for 60 seconds and start the titration. The titer will be calculated automatically with the formula "Calculation of titer in *tiamo*™". The results are being additionally regressed against the sample size and the titer 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 an aliquote of sample (see "Sample preparation for titer, blank and sample") directly into the titration vessel and add 20 mL NaCl solution, shake carefully and allow to stand for approximately **30 minutes**.

Add 10 mL deionized water and 2 mL saturated Potassium oxalate solution. Stir for 20 seconds and titrate until the third thermometric endpoint. *Tiamo*™ construct a linear regression by plotting the sample size in g (x-axis) against the difference between the third and the second endpoint (EP3-EP2) and calculates the y-intercept which represents the blank value in mL. This is automatically done by *tiamo*™ with the formula "Calculation of method blank in *tiamo*™". The blank will be saved as a common variable and has to be subtracted from each further analyzed sample.

Titration Parameters

	Titer determination	Blank determination	Phosphoric acid
Stirring rate	6	10	10
Start volume [mL]	0	0	0
Pause [s]	60	20	20
Switch off autom.	yes	yes	yes
Dosing rate [mL/min]	5	5	5
Filter factor	60	60	60
Damping until [mL]	1.0	0.1	2.0
Stop volume [mL]	5	5	5
Stop slope	off	off	off
Add. volume after stop [mL]	0.5	0.6	0.6
Evaluation start [mL]	1.0	0.1	2.0
End points [Reaction type]	ex*	1) ex* 2) ex*	1) ex* 2) ex*
EP criterion [ERC]	-0.15	1) -20 2) -30	1) -20 2) -30

* exothermic

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Sample preparation of titer, blank and sample

	Titer determination	Blank determination	Sample determination
KHP [g]	0.6 – 1.1	-	-
NaCl [mL]	-	20	20
Waiting time [min]	-	30	30
Solvent (distilled water in mL)	30	10	10
$C_2K_2O_4 \cdot H_2O$ [mL]	-	2	2
Waiting time [sec]		20	20
Sample size in gram (fertilizer)	-	0.3 – 0.7	0.61 – 0.68
Number of determination (n =)	3 - 5	3 - 5	3 - 5

Procedure for sample preparation

Pipette an aliquote of liquid fertilizer (see "Sample preparation for titer, blank and sample") directly into the titration vessel and add 20 mL NaCl solution, shake carefully and allow to stand for approximately **30 minutes**. Add 10 mL deionized water and 2 mL saturated Potassium oxalate solution. Stir for 20 seconds and titrate until the third thermometric endpoint. The H_3PO_4 content of the sample in % is automatically calculated with the formula "Calculation of phosphoric acid determination in *tiamo*™".

Results (titer and blank)

	Titer NaOH	Blank phosphoric acid sample
Endpoint 1 [mL]	2.8333	-
Endpoint 2 [mL]	-	3.2667
Endpoint 3 [mL]	-	4.9667
Difference [mL]	-	1.7000
Slope	2.5127	2.3142
Intercept [mL]	0.0217	0.0499
Correlation (R^2)	0.9994	0.9996
Molarity [mol/L]	1.9488	-
Filter factor	60	60
Titer	0.9744	-

Result (phoshoric acid sample)

	Phosphoric acid
%H_3PO_4	44.93
s(abs) %H_3PO_4	0.263
s(rel) %	0.59
n =	5

Thermometric Titration Plot (phosphoric acid sample)
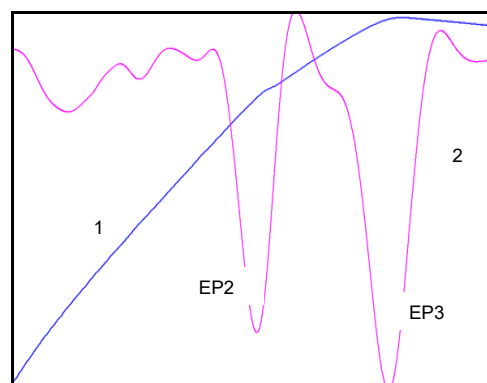
Legend:

1 = solution temperature curve

2 = second derivative curve (for endpoints)

Sample size = 0.6576 g

EP1 = 3.0250 mL   EP2 = 4.6250 mL