

Determination of total phosphate in phosphoric acid and phosphate fertilizers with thermometric titration

Of interest to: Fertilizer industry

Summary

Phosphate may be rapidly and easily titrated thermometrically using a standard solution of Mg^{2+} as titrant. The phosphate-containing solution is basified and buffered with NH_3/NH_4Cl solution prior to titration. The formation of insoluble $MgNH_4PO_4$ is exothermic. The method is a titrimetric adaptation of a classical gravimetric procedure.

This bulletin deals with the determination of phosphate in phosphoric acid and granular fertilizers such as MAP (mono-ammonium phosphate), DAP (di-ammonium phosphate) and TSP (triple superphosphate). Results are reported as percentage of P and P_2O_5 .

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

Reagents

Solvent:	deionized water
Standard:	$Na_2HPO_4 \cdot 2H_2O$ (99.5%)
Reaction solutions:	conc. HCl conc. HNO_3
Titrant:	$c(Mg(NO_3)_2) = 1 \text{ mol/L}$
Buffer NH_3/NH_4 :	87.5 g NH_4Cl + 568 mL 28% w/v NH_3 solution made to 1000mL with deionized water
Complexant:	300 g/L $K_2C_2O_4 \cdot H_2O$

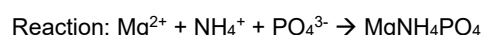
Samples

MAP 1
MAP 2
TSP
Ammoniated TSP
Phosphoric acid (plant acid)

Calculations

Titer $Mg(NO_3)_2$ with $Na_2HPO_4 \cdot 2H_2O$

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



Calculation of titer in *tiamo*TM

Assignment	RS name	Formula
RS01	EP	TET1.EP(1).VOL'
RS02	Slope	RS.EP.SLO'
RS03	Intercept	RS.EP.ITS'
RS04	Correlation (R^2)	RS.EP.COR*RS.EP.COR'
RS05	Molarity [mol/L] of titrant	(1/RS.EP.SLO')* Na_2HPO_4 .CONC'
RS06	Titer of titrant	(1/RS.EP.SLO')* Na_2HPO_4 .CONC'/TET1.CONC'
RS07	Filter factor	MV.filter factor'

Method blank

The method blank is determined by titrating different amounts of sample and plotting sample amount against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in titrant dose rate or filter factor will require a new determination of the method blank.

This parameter is stored along with the other method parameters. For all determinations, the blank volume is subtracted from the volume of titrant.

Calculation of method blank in *tiamo*TM

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

Calculation of phosphate determination in *tiamo*TM

Assignment	RS name	Formula
RS01	EP	'TET1.EP(1).VOL'
RS07	Filter factor	'MV.filter factor'
RS08	% P	('TET1.EP(1).VOL'-CV.blank')* TET1.CONC*TET1.TITER*MW.P*0.1/ MV.sample size
RS09	% P ₂ O ₅	('TET1.EP(1).VOL'-CV.blank')* TET1.CONC*TET1.TITER*MW.P ₂ O ₅ * 0.1/MV.sample size*2
RS10	Blank [mL]	'CV.blank'

Legend:

'TET1.EP(1).VOL'	= Thermometric titration end point volume
'RS.EP.SLO'	= slope for linear regression
'RS.EP.ITS'	= 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 ₂ HPO 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.P'	= 30.97376 g/mol
'MW.P ₂ O ₅ '	= 141.94452 g/mol
0.1	= factor for conversion in %
2	= correction factor

Method

Procedure for titer determination

The method is set up to automatically dispense NH₃/NH₄Cl buffer prior to the start of the titration.

Use a 10 mL Dosino to dispense a 0.5 mol/L Na₂HPO₄ standard in amounts of 2, 4, 6, 8 and 10 mL. Alternatively, aliquots of a 0.2 mol/L standard solution can be dispensed using bulb pipettes of volume 5, 10, 15, 20 and 25 mL.

Following titration of the specified number of standard Na₂HPO₄ aliquots, the titrant titer will be determined automatically using the "Calculation of titer in *tiamo*TM".

Procedure for determination of method blank

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

For MAP and DAP samples, weigh accurately a range of sample masses, from approximately 0.5 to 1.2 g directly into the titration vessels. Provide the sample vessel with a funnel with a very short stem to act as a splash trap. Add 1 mL conc. HCl, and heat on a moderate hot plate until all sample has dissolved and the mass is boiling (approximately 5 minutes). Add 2 mL deionized water through the funnel, and boil for a further 2 minutes. Cool on a water bath. Cautiously wash down the funnel and sides of the beaker with minimum deionized water and make to approximately 30 mL before titrating to a single thermometric endpoint.

In determining the method blank for phosphoric acid, it is not necessary to add HCl or heat the sample. Simply weigh samples in a range from approximately 0.4 to 1.2 g, add 30 mL deionized water and titrate.

The method blank is automatically calculated with the formula "Calculation of method blank *tiamo*TM". The intercept in mL is the method blank and can be saved as a common variable. This blank volume is subtracted from the titration volume for each sample analyzed.

Titration Parameters for phosphoric acid and fertilizer

	Titer determination Mg(NO ₃) ₂	Blank determination H ₃ PO ₄	Sample determination H ₃ PO ₄	Blank determination Fertilizer	Fertilizer MAP, DAP, (TSP)
stirring rate	10	10	10	10	10
Start volume [mL]	0.5	0.5	2.5	0.5	0.5
Pause [s]	20	20	20	120	120
Switch off autom.	yes	yes	yes	yes	yes
Dosing rate [mL/min]	6	6	6	6	6
Filter factor	30	40	40	40	40
Damping until [mL]	1	2.5	2.5	3.5	5
Stop volume [mL]	7	10	9	10	9
Stop slope	off	off	off	off	off
Add. volume after stop [mL]	off	off	off	off	off
Evaluation start [mL]	1	2.5	2.5	2	3.5
End points [Reaction type]	ex*	ex*	ex*	ex*	ex*
EP criterion [ERC]	-100	-40	-40	-40	-15

*exothermic

Procedure for sample preparation

1. MAP, DAP samples. Weigh accurately approximately 1 g sample directly into the titration vessel. Add 1 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, and continue for 5 min. Add 2 mL water and boil again for 2 min. Place on a water bath, and cool. Wash funnel with minimum deionized water. Add deionized water to approximately 30 mL and titrate with standard 1 mol/L Mg(NO₃)₂ to a single thermometric endpoint. The titration takes ~1 minute.

2. TSP samples. Weigh accurately approximately 1 g of sample, and treat with 1 mL conc. HCl and 0.33 mL conc. HNO₃ (aqua regia mixture). Heat to a gentle boil and hold for 5 min. Add 2 mL deionized water and boil for a further 2 min. Treat sample as for MAP and DAP. 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

The phosphate content of the sample in % P and % P₂O₅ is automatically calculated with the formula "Calculation of phosphate determination in **tiamo**TM"

Sample preparation for titer, blank and sample

	Titer determination	Blank determination H ₃ PO ₄	Sample determination H ₃ PO ₄	Blank determination MAP, DAP, (TSP)	Sample determination MAP, DAP,	Sample determination, TSP
Sample preparation (boiling)	-	no	no	yes	yes	yes
Na ₂ HPO ₄ . 0.5 mol/L [mL]	2 - 10	-	-	-	-	-
complexant K ₂ C ₂ O ₄ 300g/L [mL]	-	5	5	3 (5)	3 (5)	3
Buffer NH ₃ /NH ₄ Cl [mL]	5	5	5	5	5	5
Reaction solution (conc. HCl) [mL]	-	-	-	1	1	1
Reaction solution (conc. HNO ₃) [mL]	-	-	-	-	-	0.33
deion. water [mL]	to 30	to 30	to 30	to 30	to 30	to 30
Phosphoric acid [g]	-	0.4 – 1.2	1	-	-	-
Fertilizer [g]	-	-	-	0.5 - 1.2	1	1
number of determination (n =)	3-5	3-5	3-5	3-5	3-5	3-5

Results (titer and blank)

	Titer Mg(NO ₃) ₂	Blank on phosphoric acid (example)
slope	0.4629	6.6303
Intercept, mL	0.1000	0.1588
Correlation (R ²)	1.0000	1.0000
molarity [mol/L]	1.0865	-
Filter factor	30	40
titer	1.0865	-

Results

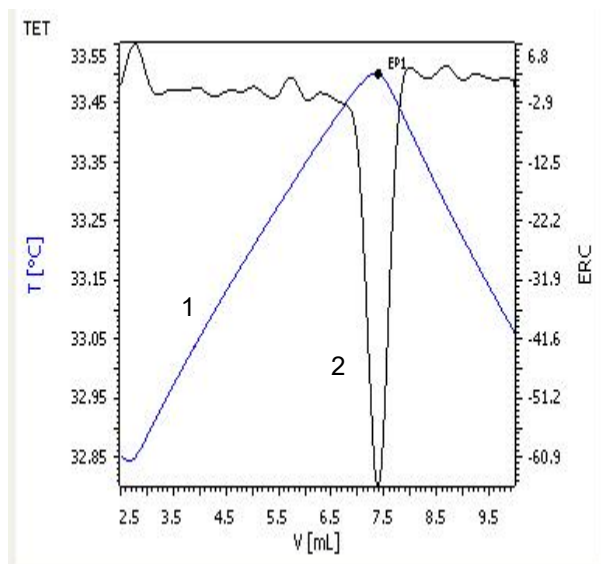
	% P	% P ₂ O ₅
Phosphoric Acid	22.19±0.04	50.85±0.08
MAP 1	22.69±0.10	51.99±0.23 (52.58)
MAP 2	23.85±0.07	54.66±0.14 (53.16)
TSP	20.36±0.04	46.66±0.09 (48.02)
Ammoniated TSP	20.54±0.15	47.06±0.34 (47.35)

Notes:

1. Titrations performed n= 6 for the phosphoric acid sample and n= 3 for all solid samples 2. Figures in

brackets represent customer results by gravimetric analysis.

Thermometric Titration Plot (Phosphoric acid)



Legend:

1 = solution temperature curve

2 = second derivative curve ("Endpoint Recognition Criterion" – ERC- curve for endpoints)