Thermo. Titr. Application Note No. H-037

Title:	Determination of Phosphate in Acid Etch Mixture

Scope:	Determination of phosphate content in an acid etching bath.

Principle:	The acid mixture is titrated with sodium hydroxide.

Sample:	Aqueous mixture of phosphoric, acetic and nitric acid
Sample Preparation:	41.398 g phosphoric acid, 10.735 g acetic acid and 6.600 g nitric acid were added to approx. 200 mL of dist. water and mixed. Then the solution was made up to 500 mL in a volumetric flask.

Reagents:	- Sodium hydroxide, 1.0 mol/L, volumetric solution, Fluka, 35256 - Potassium hydrogen phthalate, puriss. ≥ 99.5 %, Fluka, 60360 - Sodium chloride, puriss. ≥ 99.5%, Fluka 71380 - Phosphoric acid, puriss. > 85%, Fluka 79620 - Acetic acid, puriss. ≥ 99.5%, Fluka 45730 - Nitric acid, puriss. ≥ 65%, Fluka 84380

Method:	**Basic experimental parameter for phosphoric acid content:** Titrant delivery rate (mL/min): 6 No. of endothermic endpoints: 3 Data smoothing factor: 90 **Procedure:** The sample solution was dosed in the titration vessel and sodium chloride solution (265 g/L) was added in order to make sure that the thermoprobe was immersed in the solution. After 5 sec of stirring the sample was titrated with *c*(NaOH) = 1.0 mol/L to the third exothermic endpoint (EP3). **Determination of the method blank:** Aliquots of 1.0, 1.5, 2.0, 2.5 and 3.0 mL of the sample solution were titrated. A linear regression was carried out, plotting the aliquots volume on the x-axis and the volume of the used titrant on the y-axis. The y-intercept represents the method blank in mL, and has to be subtracted from all titrated volumes. **Titer determination of NaOH:** Potassium hydrogen phthalate was dried for 2 hours at 140℃ and cooled down in a desiccator. 5 amounts ranging from approximately 0.6 to 1.4 g were weighed in roughly equal increments directly into the titration vessels. Dist. water was added in order to make sure that the thermoprobe was immersed in the solution and the titration started. The sample size was then plotted on the x-axis with corresponding volumes of titrant on the y-axis. A linear regression was performed. The molarity of the NaOH-solution is the reciprocal of the gradient. In this instance, the y-intercept was not used as the method blank, due to the need to match the sample matrix.

Results:

Sample size [mL]	HNO_3 %w/v	HOAc %w/v	H_3PO_4 %w/v
3.0	0.90	2.17	6.89
3.0	0.97	2.17	6.80
3.0	0.95	2.11	6.91
3.0	0.90	2.12	6.94
3.0	0.90	2.13	6.91
3.0	0.92	2.11	6.91
3.0	0.96	2.19	6.81
3.0	0.87	2.11	6.94
3.0	0.84	2.13	6.96
3.0	0.88	2.06	6.99
Mean value	0.91	2.13	6.91
SD	0.042	0.032	0.056
RSD	4.67%	1.51%	0.80%

Fig. 1: Results of phosphate determination

Determination of Method Blank:
(see Fig. 1)

Sample size [mL]	Volume of NaOH [mL]
3.0	6.96
3.0	6.83
3.0	6.89
2.5	6.98
2.5	6.98
2.5	6.90
2.0	6.96
2.0	7.00
2.0	6.96
1.5	6.90
1.5	6.98
1.5	7.09
1.0	7.14
1.0	7.24
1.0	7.15

Fig. 2: Results of method blank determination

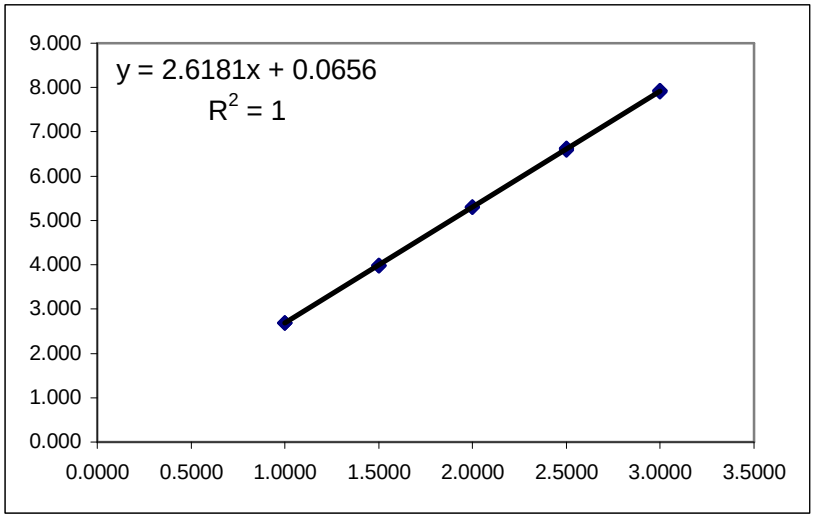


Fig. 3: Regression analysis to determine method blank
y-intercept = method blank

Titer determination of NaOH:

(See Fig. 5)

Sample size [mg]	Sample size [mmol]	Volume of NaOH [mL]	Titer of NaOH
0.5983	2.930	2.937	1.0025
0.6060	2.977	2.983	0.9999
0.6070	2.972	2.979	1.0029
0.8146	3.999	4.002	1.0005
0.8127	3.989	3.996	0.9996
0.7964	3.903	3.906	1.0022
1.0157	4.970	4.978	1.0021
0.9943	4.879	4.879	1.0010
1.0079	4.945	4.946	1.0009
1.1963	5.868	5.865	1.0013
1.1998	5.875	5.819	1.0123
1.2177	5.962	5.973	1.0008
1.3983	6.857	6.861	1.0002
1.4030	6.870	6.893	0.9989
1.4024	6.877	6.885	0.9995
		Mean value	1.0018
		SD	0.0032
		RSD	0.32 %

Fig. 4: Results of titer determination

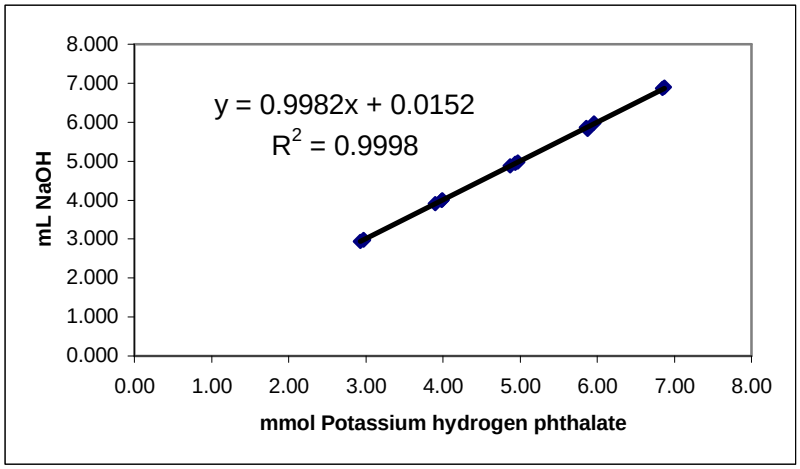


Fig. 5: Regression analysis to determine the concentration of NaOH
Molarity = 1/gradient = 1/0.9982 = 1.0018 mol/L

Calculation:

$$Titer\ \ NaOH\ \ = \frac{Sample\ \ \ size\ \times 1000}{EP\,1\times Conc\ \ (NaOH\ \ \ )\times MW\ \ (C_8H_5KO_4)}$$

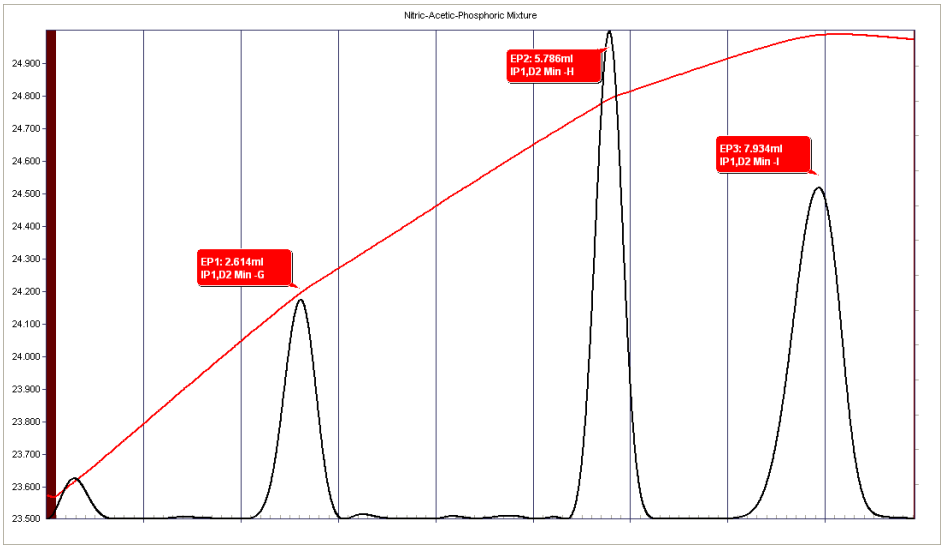
$$H_3PO_4\ (\%w/v) = \frac{(EP3-EP2)\times Conc\,(NaOH\,)\times Titer\,(NaOH\,)\times MW\,(H_3PO_4)\times 100}{Sample\ size\times 1000}$$

$$HOAc\ (\%w/v) = \frac{((EP2-EP1)-(EP3-EP2))\times Conc(NaOH\,)\times Titer(NaOH\,)\times MW\,(HOAc)\times 100}{Sample\ size\times 1000}$$

$$HNO_3\ (\%w/v) = \frac{((EP1-blank\,)-(EP3-EP2))\times Conc\,(NaOH\,)\times Titer\,(NaOH\,)\times MW\,(HNO_3)\times 100}{Sample\ \ size\times 1000}$$

with:

EP1	= First endpoint of phosphate determination
EP2	= Second endpoint of phosphate determination
EP3	= Third endpoint of phosphate determination
blank	= Method blank
Conc(NaOH)	= Concentration of the NaOH solution
Titer(NaOH)	= Titer of the NaOH solution
MW(x)	= Molecular weight of the analyte
100	= Calculation factor for %
1000	= Conversion factor for L

Thermometric Titration Plot:	 **Fig. 6:** Example curve Legend: Red = solution temperature curve Black = second derivative curve Brown area = Endpoints in this area are ignored