Thermo. Titr. Application Note No. H-084

Title:	**Determination of Sulfuric, Phosphoric and Nitric Acid Mixtures**

***Scope*:**	Determination of mixtures of sulfuric, phosphoric, and nitric acids. The procedure is suitable for automated analysis using a 814 Sample Processor.

Principle:

1. Titration of sulfate with barium chloride to obtain sulfuric acid content.
2. Titration with standard sodium hydroxide to obtain two endpoints:

Endpoint 1	Endpoint 2
HNO_3 (pKa = -1.4)	H_3PO_4 (pKa_2 = 7.21)
HCl (because SO_4^{2-} precipitated with $BaCl_2$) (pKa~-1)	
H_3PO_4 (pKa_1 = 2.14)	

3. Calculate result from Endpoint 1 as “Total Acid” expressed as HNO_3.
4. Calculate result from Endpoint 2 as phosphoric acid.
5. To obtain nitric acid content, convert phosphoric and sulfuric acid results to nitric acid equivalent, and subtract from Total Acids content.

Reagents:	2 mol/L NaOH (standardized) 1 mol/L $BaCl_2$ (standardized)

Method:	Basic Experimental Parameters:	
	Titrant delivery rate (mL/min.)	4
	Data smoothing factors:	
	- sulfuric acid titration	60
	- total acids/phosphoric titration	90
	Stirring speed	15

Procedure: *The following procedure has been applied to an acid mixture comprising approximately 15% H_3PO_4 and 20% each H_2SO_4 and HNO_3.*

Weigh accurately 1.5 – 1.6g acid mixture into a titration vessel, and add 35mL DI water.

Titrate with a titration program, where the method for determination of sulfuric acid by $BaCl_2$ titration is performed first and „chained“ to the total acids/phosphoric acid titration. The sulfuric acid titration is set to stop automatically after the endpoint has been resolved. The total acids/phosphoric acid titration then starts automatically, and the automatic stop function is activated after the second endpoint has been resolved.

When setting up the 814 automation program, it is only necessary to select the first titration method, the sulfuric acid determination.

To obtain accurate results, it is necessary to determine titration blank values for the sulfuric acid titration, and the total acids/phosphoric titration. Moreover, it has been found necessary to determine a blank value for the difference between the first and second endpoints, which is used to compute the phosphoric acid content. In the example illustrate here, masses of acid ranging between approximately 1 – 1.7g were weighed and titrated. The mass of acid (x-axis) was plotted against the volume of titrant consumed (y-axis), and the blank value (the y-intercept) computed by regression analysis.

Results:

Acid	**% by mass**
Total acids (as HNO_3)	56.1±0.08 (n=11)
H_2SO_4	21.2±0.04 (n=11)
H_3PO_4	15.4±0.12 (n=11)
HNO_3	19.0±0.15 (n=11)

Calculations:

1. Sulfuric acid titration:

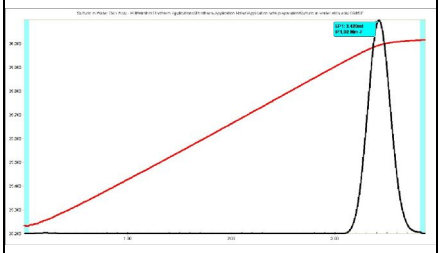
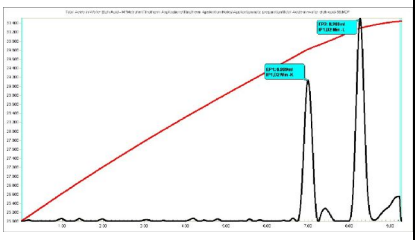
$$H_2SO_4\ \%ww = \frac{((EP - blank1) \times M\,BaCl_2 \times 97.96738)}{(\text{sample mass, g} \times 10)}$$

2. Total acids/phosphoric titration:

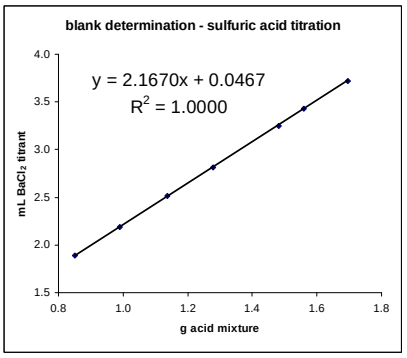
$$\text{Total acids (as } HNO_3)\ \%w/w = \frac{((EP1 - blank2) \times M\,NaOH \times 62.99564)}{(\text{sample mass, g} \times 10)}$$

$$H_3PO_4\ \%w/w = \frac{((EP3 - EP2 - blank3) \times M\,NaOH \times 97.9769)}{(\text{sample mass, g} \times 10)}$$

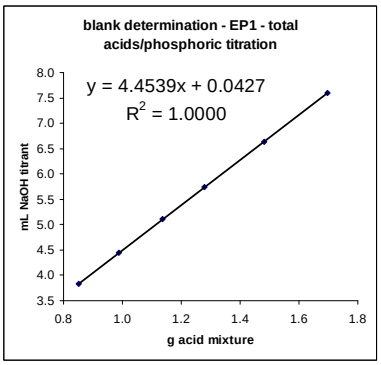
$$HNO_3\ \%w/w = \%\ \text{Total Acids} - \frac{\%\ H_3PO_4 \times 62.99564}{97.9769} - \frac{\%\ H_2SO_4 \times 62.99564 \times 2}{97.96738}$$

Titration Plots:	*Legend: red = solution temperature, black = second derivative (endpoint) curve*	
		
	Sulphuric acid titration	*Total acids/phosphoric acid titration*

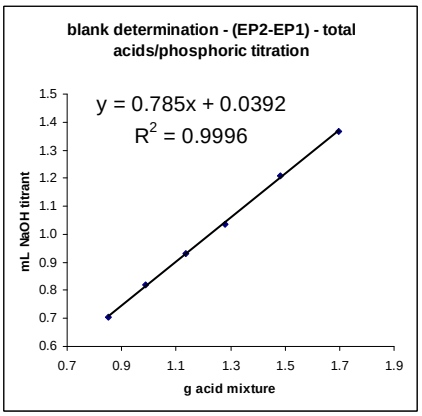
Blank determinations:



H_2SO_4 determination:
blank = 0.0467mL



Total acids determination:
blank = 0.0427mL



H_3PO_4 determination:
blank = 0.0392mL