Thermo. Titr. Application Note No. H-038

Title:	Determination of Sulfate and Total Acids in Nitrating Mixture

Scope:	Determination of Sulfate and Total Acids in Nitrating Mixture

Principle:	In a first titration the sulfate content of the sample solution is determined, followed by the determination of the total acids.

Sample:	Aqueous mixture of sulfuric and nitric acid
Sample Preparation:	20.817 g sulfuric acid and 19.478 g nitric acid were added to approx. 100 mL of dist. water and mixed. Then the solution was made up to 200 mL in a volumetric flask.

Reagents:	- Sodium hydroxide, 1.0 mol/L, volumetric solution, Fluka, 35256 - Barium chloride dihydrate, puriss. ≥ 99.0 %, Fluka, 11760 - Potassium hydrogen phthalate, puriss. ≥ 99.5 %, Fluka, 60360 - Sodium sulfate, puriss. ≥ 99.0 %, Fluka, 71960 - Sulfuric acid, 95 – 97 %, Fluka, 84720 - Nitric acid, 65 %, Fluka, 84380

Method:	**Basic experimental parameters for sulfate determination:** Titrant delivery rate (mL/min): 2 No. of endothermic endpoints: 1 Data smoothing factor: 76 **Procedure:** 2 mL of the sample solution were pipetted in the titration vessel and approximately 25 mL dist. water were added. After 5 sec of stirring the sample was titrated with *c*($BaCl_2$) = 1.0 mol/L to an exothermic endpoint (EP1a). **Basic Experimental Parameters for total acids determination:** Titrant delivery rate (mL/min): 3 No. of endothermic endpoints 1 Data smoothing factor: 50 **Procedure:** The titration was carried out in the same titration vessel and with the same sample as the sulfate determination. The sample was titrated with *c*(NaOH) = 1.0 mol/L to an exothermic endpoint (EP1b). **Determination of the method blank:** Aliquots of 0.5, 1.0, 1.5, 2.0 and 2.5 mL of the sample solution were titrated. A linear regression was carried out, plotting aliquots volume on the x-axis and the volumes of the two different titrants 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 105°C and cooled down in a desiccator. Five samples of approximately 0.6 to 1.4 g were weighed in nearly equal increments directly into the titration vessels. Before starting the titration approximately 25 mL dist. water were added. 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. **Titer determination of $BaCl_2$:** Sodium sulfate was dried over night at 140℃ and co oled down in a desiccator. Five samples ranging from 0.25 to 0.5 g were weighed in roughly equal increments directly into the titration vessels. Before starting the titration approximately 25 mL dist. water were added. 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 $BaCl_2$-solution is the reciprocal of the gradient. Again the y-intercept was not used as the method blank.

Results:

Sample size [mL]	SO_4 [g/L]	H_2SO_4 %w/v	HNO_3 %w/v
2.0	107.35	10.96	4.82
2.0	108.54	11.08	4.83
2.0	109.39	11.17	4.65
2.0	108.34	11.06	4.84
2.0	108.88	11.12	4.82
2.0	108.07	11.03	4.82
2.0	109.56	11.19	4.94
2.0	110.68	11.30	4.92
2.0	110.11	11.24	4.88
2.0	108.17	11.04	4.95
Mean value	108.91	11.12	4.85
SD	1.02	0.10	0.09
RSD	1.77 %	0.94 %	1.77%

Determination of Method Blank:
(see Fig. 1)

Sample size [mL]	Volume of $BaCl_2$ [mL]	Volume of NaOH [mL]
2.5	2.839	7.923
2.5	2.850	7.880
2.5	2.839	7.892
2.0	2.275	6.315
2.0	2.303	6.370
2.0	2.287	6.343
1.5	1.747	4.791
1.5	1.755	4.823
1.5	1.754	4.817
1.0	1.221	3.324
1.0	1.220	3.303
1.0	1.203	3.298
0.5	0.674	1.773
0.5	0.693	1.786
0.5	0.695	1.792

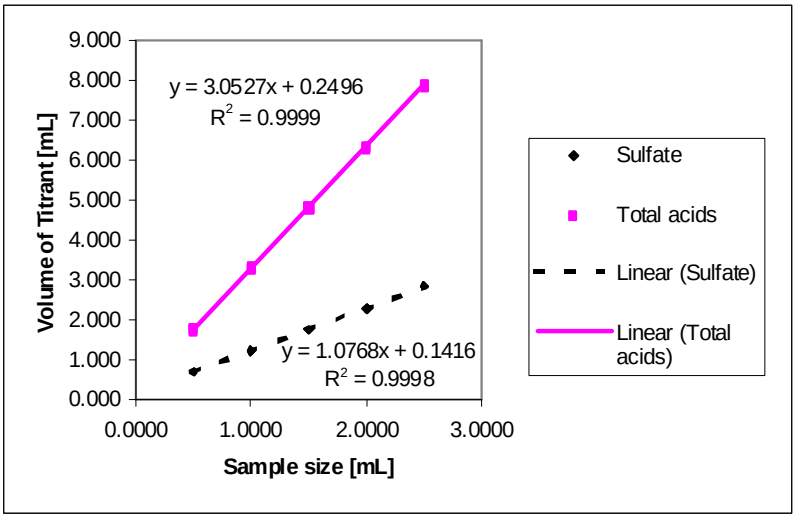


Fig. 1: Regression analysis to determine method blank
y-intercept = method blank
blank a = Sulfate determination
blank b = Total acids determination

Titer determination of $BaCl_2$:

(See Fig. 2)

Sample size [mg]	Sample size [mmol]	Volume of $BaCl_2$ [mL]	Titer of $BaCl_2$
0.2414	1.693	1.681	1.0588
0.2481	1.740	1.721	1.0620
0.2410	1.690	1.671	1.0637
0.3001	2.105	2.064	1.0621
0.3035	2.129	2.083	1.0637
0.3028	2.124	2.085	1.0602
0.3501	2.456	2.405	1.0570
0.3496	2.452	2.399	1.0582
0.3502	2.456	2.406	1.0570
0.4027	2.825	2.744	1.0611
0.3993	2.801	2.726	1.0593
0.4002	2.807	2.735	1.0582
0.4505	3.160	3.063	1.0599
0.4491	3.150	3.052	1.0607
0.4499	3.156	3.045	1.0652
		Mean value	1.0605
		SD	0.0025
		RSD	0.24 %

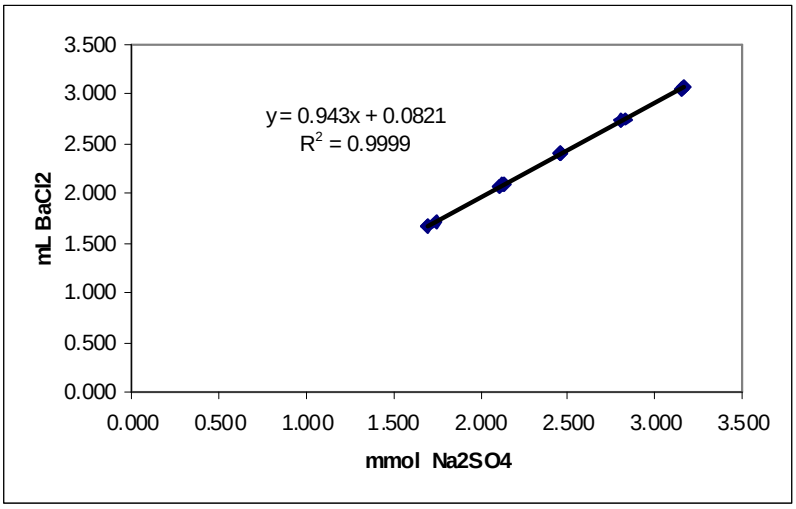


Fig. 2: Regression analysis to determine the concentration of $BaCl_2$
Molarity = 1/gradient = 1/0.943 = 1.0604 mol/L

Titer determination of NaOH:

(See Fig. 3)

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 **SD** **RSD**	1.0018 0.0032 0.32 %

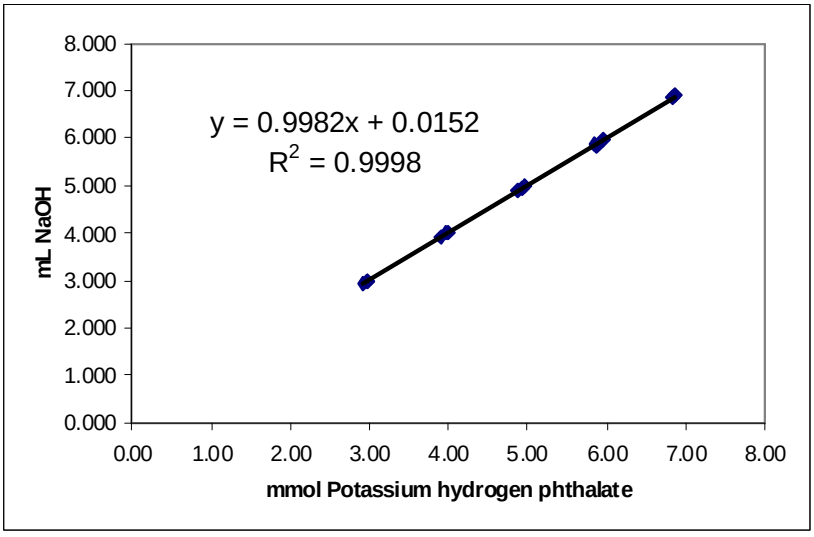


Fig. 3: Regression analysis to determine the concentration of NaOH
Molarity = 1/gradient = 1/0.9982 = 1.0018 mol/L

Calculation:

$$Titer\ BaCl_2 = \frac{Sample\ size \times 1000}{(EP1a - blank\ a) \times Conc(BaCl_2) \times MW(Na_2SO_4)}$$

$$SO_4^{2-}[g/L] = \frac{(EP1a - blank\ a) \times Conc(BaCl_2) \times Titer(BaCl_2) \times MW(SO_4^{2-})}{Sample\ size}$$

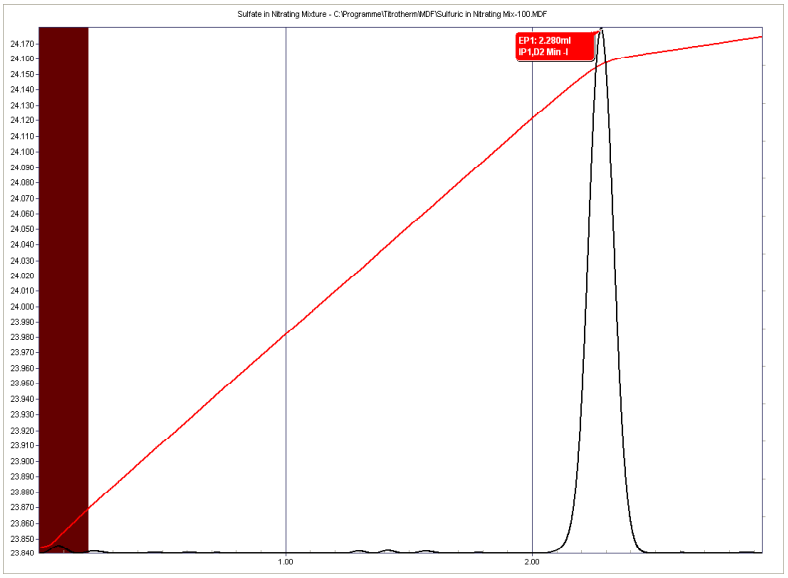
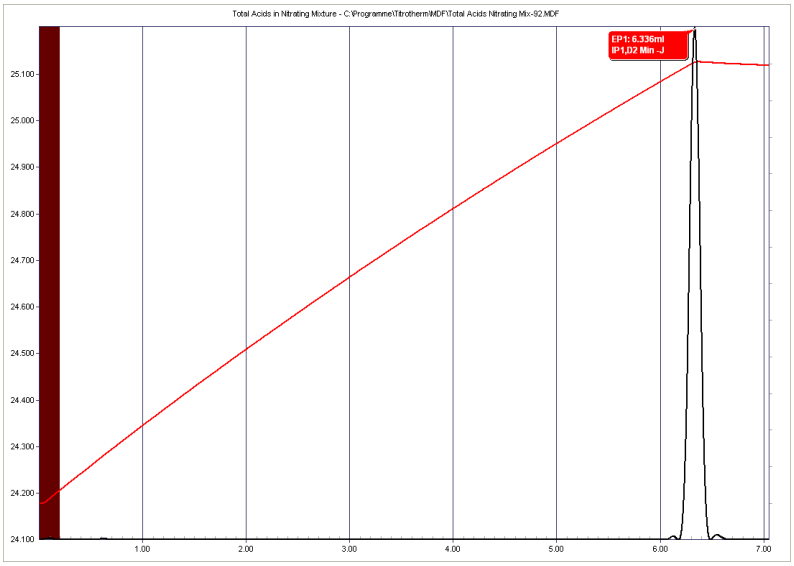
$$H_2SO_4\ (\%w/v) = \frac{(EP1a - blank\ a) \times Conc(BaCl_2) \times Titer(BaCl_2) \times MW(H_2SO_4) \times 100}{Sample\ size \times 1000}$$

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

$$HNO_3\ (\%w/v) = \frac{\frac{(EP1b - blank\ b) - (EP1a - blank\ a) \times 2 \times Conc(NaOH)}{Conc(BaCl_2)} \times Titer(BaCl_2) \times MW(H_2SO_4) \times 100}{Sample\ size \times 1000}$$

with:

EP1a	= Endpoint from sulfate determination
Blank a	= Method blank sulfate determination
EP1b	= Endpoint total acids determination
Blank b	= Method blank total acids determination
Conc(x)	= Concentration of the used titrant
Titer(x)	= Titer of the used titrant
MW(x)	= Molecular weight of the analyte
100	= Calculation factor for %
1000	= Conversion factor for L

Thermometric Titration Plot:	 Example curve of a sulfate determination  Example curve of a total acids determination Legend: Red = solution temperature curve Black = second derivative curve Brown area = Endpoints in this area are ignored