Thermo. Titr. Application Note No. H-009

Title:	**Determination of Sulfate in Brines**

***Scope*:**	Determination of the sulfate content of brines

***Principle*:**	An aliquot of brine is acidified with nitric acid and titrated with standard barium chloride solution to a single thermometric endpoint. In concentrated brines, the endpoint is subject to some rounding. For accurate results, it is necessary to determine the method blank on aliquots of a sample brine solution.

Reagents:	Standard 1mol/L $BaCl_2$ solution 5 mol/L HNO_3 Anhydrous Na_2SO_4 A.R.

Method:	Basic Experimental Parameters: Data rate (per second) 10 Titrant delivery rate (mL/min.) 2 No. of endothermic endpoints 1 Data smoothing factor 55 Procedure: Pipette a 25.00 mL or 50mL aliquot of brine into a titration vessel. Add 1 mL 5 mol/L HNO_3, and titrate with 1mol/L $BaCl_2$ solution to an exothermic endpoint. Determination of method blank: Titrate aliquots of 20, 25, 30, 40 and 50mL of a selected typical brine sample according to Section 4.2. Subject the results to regression analysis, plotting aliquot volume on the x-axis and $BaCl_2$ titre on the y-axis. The y-intercept is the method blank in mL, and must be subtracted from all titres. It will be noted in the example given here; the intercept is negative, meaning that this amount must be effectively <u>*added*</u> to the titre. Standardization of $BaCl_2$ titrant: Dry anhydrous A.R. Na_2SO_4 for 2 hours at 200ºC. Cool in a dessicator. Weigh accurately 5 amounts ranging from approximately 0.13g to 0.65g in roughly equal increments directly into titration vessels. Add 30mL D.I. water and 1 mL 5 mol/L HNO_3 and titrate. Convert masses of Na_2SO_4 titrated to mmole, and plot on the x-axis, with

corresponding titres of $BaCl_2$ on the y-axis. Perform a regression analysis, and compute the gradient of the regression curve. The molarity of the $BaCl_2$ is the reciprocal of the gradient. In this instance, the y-intercept is not used as the method blank, due to the need to *match the sample matrix.*

Results (Example): Analysis of brines:

Sample No.	Sample Aliquot, mL	Sulfate as SO_4^{2-}, g/L
1	50	4.73. 4.75 φ = 4.74
2	20 - 50	12.16, 12.13, 12.17, 12.14, 12.08 φ = 12.14, S.D. = 0.033
3	50	2.80, 2.77 φ = 2.79
4	25	7.70, 7.70 φ = 7.70
5	25 & 50	3.10, 3.14, 3.11 φ = 3.12

Determination of Method Blank (Example based on sample #2)

(see Fig. 1)

Sample aliquot volume, mL	Titre $BaCl_2$, mL
20	2.533
25	3.155
30	3.792
40	5.032
50	6.330

Standardization of $BaCl_2$ Titrant

(see Fig. 2)

Mass of Na_2SO_4 g	*Equiv. mmole Na_2SO_4	$BaCl_2$ titre, mL
0.1320	0.925	1.012
0.2690	1.884	1.971
0.5444	3.813	3.909
0.4119	2.885	2.986
0.6662	4.667	4.751

** Assumes reagent purity of 99.5%*

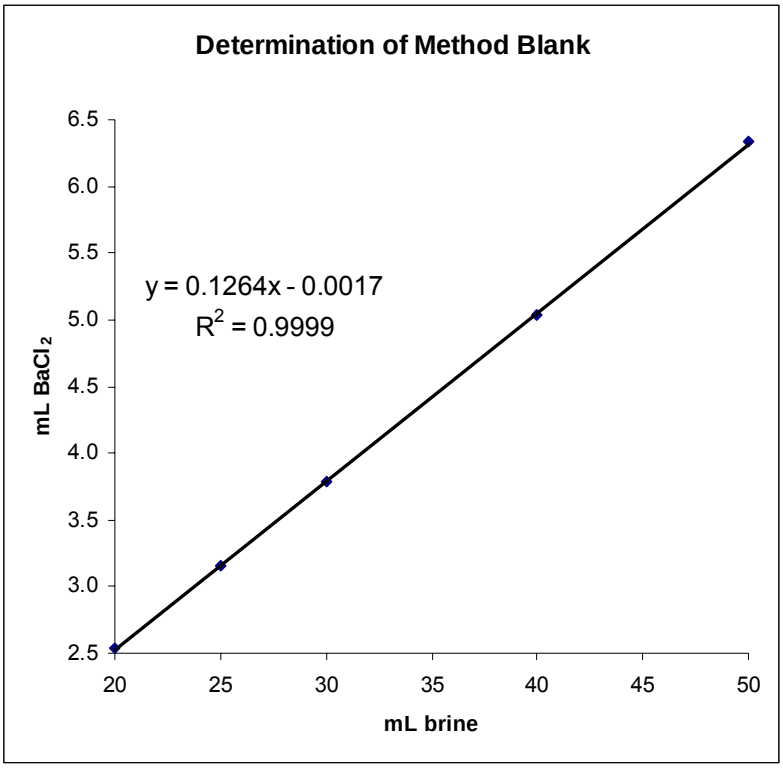


Fig.1. Regression analysis to determine method blank
y-intercept = method blank = -0.0017mL

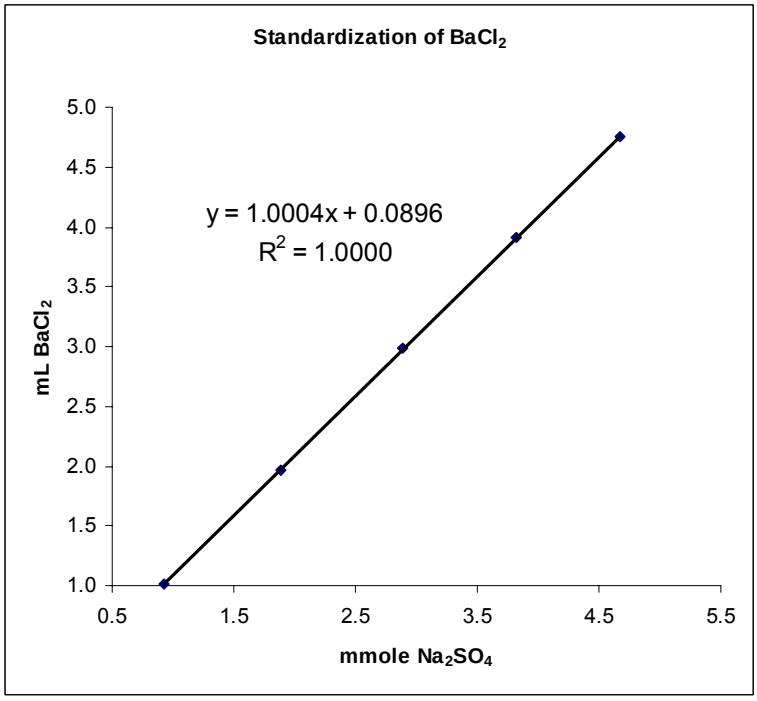


Fig. 2. Regression analysis to standardize $BaCl_2$
Molarity = 1/gradient = 1/1.0004 = 0.9996 mol/L

Calculation:

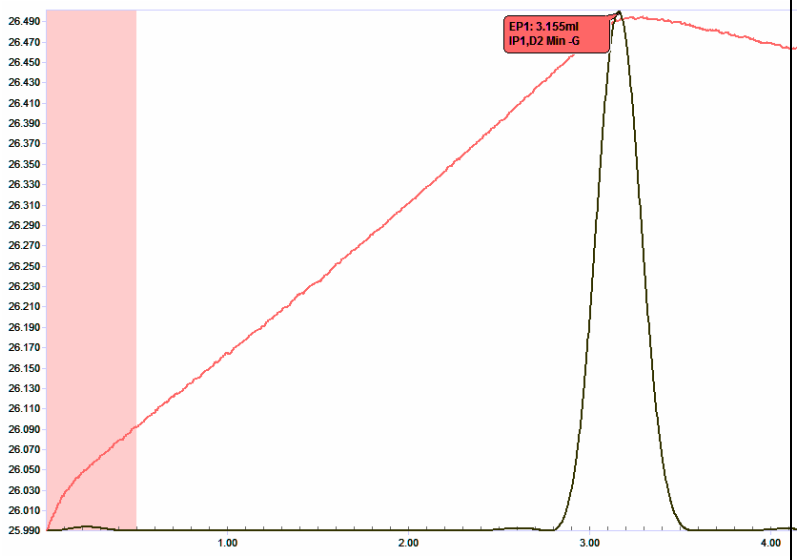
$$SO_4^{2-}\ g/L = \frac{((titre, mL - blank, mL) \times M\ BaCl_2 \times FW\ SO_4^{2-})}{sample\ volume, mL}$$

Example:

$$SO_4^{2-}\ g/L = \frac{((2.004 - (-0.0017)) \times 0.9996 \times 96.058)}{25.00}$$

$$= 7.70$$

Thermometric Titration Plot:



Legend:

Red = solution temperature curve

Black = second derivative curve