

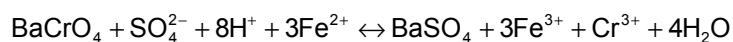
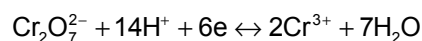
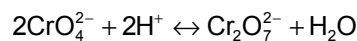
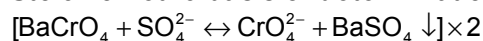
## Thermo. Titr. Application Note No. H-031

**Title:** Determination of Low Levels of Sulfate by Barium Chromate Displacement

**Scope:** Determination of low levels of sulfate (to approximately 20mg/L  $\text{SO}_4^{2-}$ ) by thermometric titration.

**Principle:** Sulfate is precipitated by reaction with an acidified barium chromate solution. Excess barium chromate is precipitated by basification with ammonia solution. Residual soluble chromate equivalent to the sulfate content of the sample is titrated with a solution of standard ferrous ion to a thermometrically-determined endpoint.

*Stoichiometric basis of determination:*



*Thus: 3mole  $\text{Fe}^{2+} \equiv 1 \text{mole } \text{SO}_4^{2-}$ .*

Reference:

Margaret D. Foster. Volumetric determination of sulfate in water: the barium chromate method. *Ind. Eng. Chem. Anal. Ed*; **8**(3) 1936, 195-6

**Reagents:**

- 0.1 mol/L ammonium iron(II) sulfate solution, prepared by dissolution in DI water acidified 1:10 with 10% w/v sulfuric acid solution
- 7.5 g/L barium chromate (re-precipitated) in 0.25mol/L HCl
- 10% w/v sulfuric acid solution
- 1 mol/L hydrochloric acid
- concentrated ammonia solution

sulfate test solution: 0.0796g of anhydrous sodium sulfate was dissolved in and made to 500mL with DI water in a volumetric flask. This is equivalent to 107.7mg/L  $\text{SO}_4^{2-}$ .

**Method:**

## Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	2
No. of exothermic endpoints	1
Data smoothing factor	40
Stirring speed (802 stirrer)	6
Delay before start (secs.)	60

Pipette 100mL of water containing sulfate in the range 25-250mg/L  $\text{SO}_4^{2-}$  into a 250mL beaker containing a magnetic spin bar. Acidify with 1 mol/L hydrochloric acid using 1 drop methyl orange indicator. Place on a magnetic stirrer, and add 10mL of barium chromate. Stir for 10 minutes.

Precipitate the residual barium in solution as barium chromate by basification with ammonia solution. The suspension will turn a pale lemon yellow. Add approximately 8 drops of ammonia past this point. Stir for another 5 minutes to assist in coagulating the precipitate.

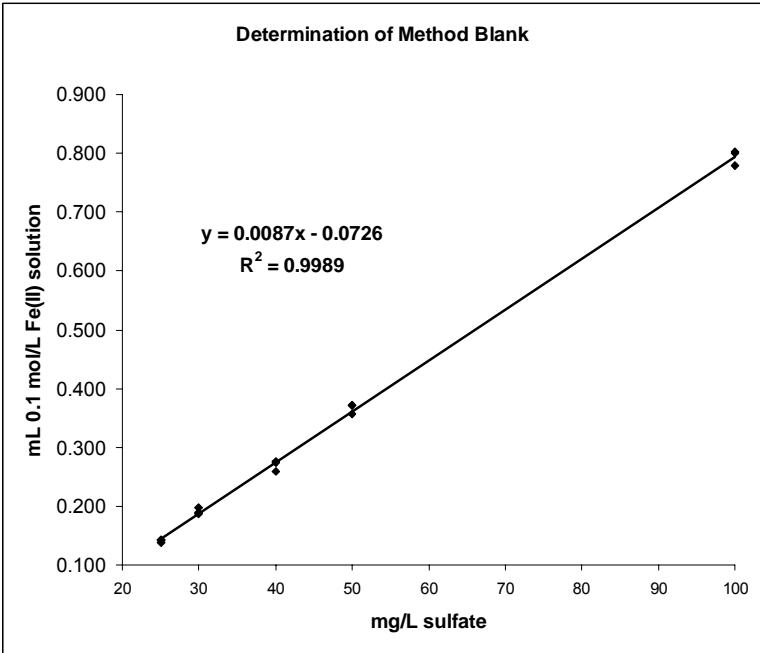
Transfer quantitatively to a 200mL volumetric flask, making to volume with DI water. Filter through a dry filter paper (Whatman 5, 6, 40, 42 or equivalent), and collect approximately 150mL of filtrate – sufficient for duplicate 50mL aliquots.

Pipette a 50mL aliquot into a titration vessel, and titrate with a program that adds a pre-dose of 5mL 10% w/v sulfuric acid, and allows an equilibration time of 60 seconds before the titration commences. This long equilibration time is necessary because of the extremely low temperature rise that may be observed (as little as 0.001K at low levels of sulfate).

*Note: it is important to determine the method blank for each new batch of barium chromate solution that has been prepared.*

<b>Example:</b> Analysis of sodium sulfate test solution, nominal 107.7mg/L SO <sub>4</sub> <sup>2-</sup>			
<i>Different aliquots of sulfate test solution were taken to simulate a range of sulfate concentrations in natural waters.</i>	Aliquot test soln. mL	Nominal SO <sub>4</sub> <sup>2-</sup> conc. mg/L	Analyzed SO <sub>4</sub> <sup>2-</sup> conc. mg/L
	25	26.9	26.5, 26.0, 26.4 φ = 26.3
	30	32.3	33.2, 31.9, 32.3 φ = 32.4
	40	43.1	42.9, 42.8, 41.0 φ = 42.2
	50	53.9	54.7, 53.0, 54.7 φ = 54.1
	100	107.7	104.8, 107.9, 107.4 φ= 106.7

<b>Calculation:</b>
$\text{mg/L SO}_4^{2-} = ((\text{titre-blank}) * \text{mol/L Fe(II)} * 96.064 * 1000) / 75$

<b>Determination of method blank:</b>	Results from the above sample were used in the regression analysis. The method blank is -0.0726mL, i.e., 0.0726mL must be <u>added</u> to the titre in this instance.
<p><i>The method blank is determined in setting up any thermometric titration method. However, in this case it is doubly important as:</i></p> <ul style="list-style-type: none"> <li>• <i>Barium chromate is slightly soluble under the method conditions.</i></li> <li>• <i>The Ba<sup>2+</sup>:CrO<sub>4</sub><sup>2-</sup> stoichiometry cannot be presumed to be exact in commercially-available salt.</i></li> </ul>	

**Thermometric Titration Plot:**

**Legend:**

*Red = solution temperature curve*

*Black = second derivative curve*

