Ω Metrohm
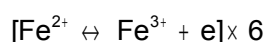
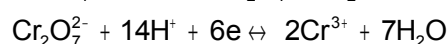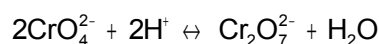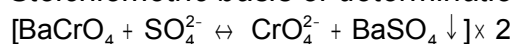# Thermo. Titr. Application Note No. H-110

Title:	Determination of Sulfate in Drinking Water by Barium Chromate Displacement

Scope:	Determination of sulfate in drinking waters (to approximately 10mg/L SO_4^{2-}) by thermometric titration.

Principle:	Sulfate is precipitated by reaction with an acidified barium chromate solution. The 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:

$$[BaCrO_4 + SO_4^{2-} \leftrightarrow CrO_4^{2-} + BaSO_4 \downarrow] \times 2$$

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \leftrightarrow 2Cr^{3+} + 7H_2O$$

$$[Fe^{2+} \leftrightarrow Fe^{3+} + e] \times 6$$

$$BaCrO_4 + SO_4^{2-} + 8H^+ + 3Fe^{2+} \leftrightarrow BaSO_4 + 3Fe^{3+} + Cr^{3+} + 4H_2O$$
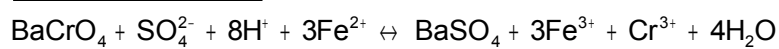
Thus: 3mole Fe^{2+} ≡1 mole SO_4^{2-}

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:	$c((NH_4)_2SO_4.FeSO_4.6H_2O)$ = 0.1 mol/L, prepared by dissolution in DI water and acidified 1:10 with 25% v/v sulfuric acid solution

$c(BaCrO_4)$ = 7.5 g/L barium chromate in $c(HCl)$ = 0.25 mol/L

$c(H_2SO_4)$ = 25% v/v

HCl, concentrated

NH_3 solution, concentrated

Phenolpthalein indicator solution, 0.1% w/v in ethanol

$c(K_2Cr_2O_7)$ = 0.01 mol/L standard solution, prepared from $c(K_2Cr_2O_7)$ = 0.1 mol/L stock solution

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Method:	Basic Experimental Parameters:

Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	4
No. of exothermic endpoints	1
Data smoothing factor	30
Stirring speed (802 stirrer)	9
Delay before start (secs.)	60

Pipette 200mL of water containing sulfate in the range 25-250mg/L SO_4^{2-} into a 250mL beaker containing a magnetic spin bar. Acidify with 10 drops concentrated hydrochloric acid. Place on a magentic stirrer, and add 10mL of barium chromate. Stir for 20 minutes (the precipitate of $BaSO_4$ can take some time to form and to mature).

Add 5 drops phenolphthalein solution and precipitate the residual barium in solution as barium chromate by basification with ammonia solution.The suspension will turn a pale orange colour. Add approximately 8 drops of ammonia past this point. Stir for another 10 minutes to assist in coagulating the precipitate.

Transfer quantitatively to a 250mL volumetric flask, making to volume with DI water. Filter through a dry Whatman No. 2 filter paper , and collect approximately 200mL of filtrate – sufficient for triplicate 50mL aliquots if required.

Note: it is important that the filtered residue in the filter paper has a pale yellow colour. This indicates the presence of BaCrO$_4$, which demonstrates that a satisfactory excess of BaCrO$_4$ has been added to the original solution. If the precipitate is white, then this indicates that insufficient BaCrO$_4$ has been added. The determination must be repeated, using either a smaller amount of salt or a larger volume of BaCrO$_4$ solution.

Pipette a 50mL aliquot into a titration vessel. This contains 40mL of original water. Add 5mL $c(H_2SO_4)$ = 25% v/v. .Allow a delay 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. *Note that for titrant volumes less than 0.5mL, damping should be reduced to zero, and the filter factor to 15.*

Standardization of $c((NH_4)_2SO_4.FeSO_4.6H_2O)$ = 0.1 mol/L titrant:
Prepare a 10mL Dosino with $c(K_2Cr_2O_7)$ = 0.01 mol/L solution. Prepare titration vessels with 5mL $c(H_2SO_4)$ =

25% v/v and 30 mL DI water. Prepare a titration program using the above parameters, but with the addition of a dosing step to dispense the $K_2Cr_2O_7$ solution. Conduct titrations with 1, 2, 3, 4, 5, 6 and 7mL $K_2Cr_2O_7$ solution. The method calculations will determine the slope and intercepts of the regression curve, the titrant molarity, and the mmol of standard $K_2Cr_2O_7$ solution dispensed at each aliquot. The y-intercept value shall serve as the method blank in this determination, and may be stored as a common variable.

Examples:

Sample	mg/L SO_4
Brisbane (North Pine) tap water, collected 02/02/11	55.8, 55.8, 55.8 Av = 55.8
„Frantelle" brand bottled water	11.2, 11.2, 11.2 Av = 11.2

Calculation:

$$mg/L\ SO_4 = \frac{(EP, mL - blank, mL) * c(Fe(II) * 96.0626 * 1000)}{(sample\ vol., mL * 3)}$$

(sample vol. = 40mL for this determination)

Standardization

Nominal $c((NH_4)_2SO_4.FeSO_4.6H_2O) = 0.1$ mol/L, standard = $c(K_2Cr_2O_7) = 0.01$ mol/L

Slope = 0.6188
Intercept = 0.0286 mL
R^2 = 1.0000
Molarity = 0.0970
(Molarity = $6*c(K_2Cr_2O_7)/slope$)

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Thermometric titration plots

Legend:
blue = solution temperature
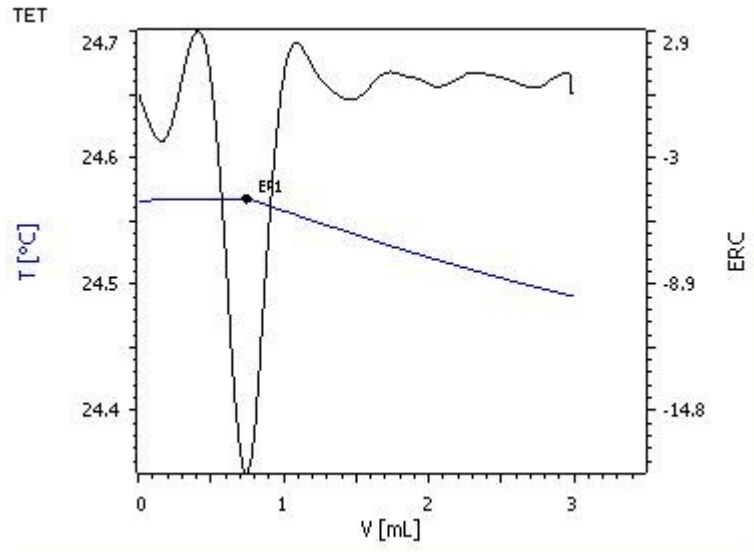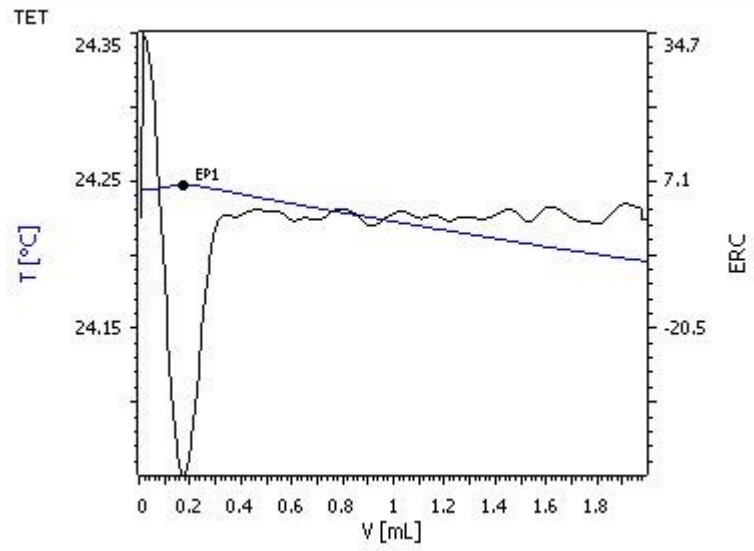black = ERC (2nd derivative)

Fig. 1. Brisbane tap water (55.8 mg/L SO_4)

Fig. 2. „Frantelle" bottled water (11.2 mg/L SO_4)