

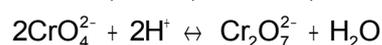
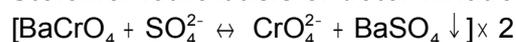
Thermo. Titr. Application Note No. H-111

Title: Determination of Sulfate in Harvested Salt

Scope: Determination of sulfate in harvested common salt to approximately 0.01% SO₄.

Principle: Sulfate is precipitated as barium sulfate 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:



Thus: 3 mol Fe²⁺ ≡ 1 mole SO₄²⁻

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((NH₄)₂SO₄·FeSO₄·6H₂O) = 0.1 mol/L, prepared by dissolution in DI water and acidified 1:10 with 25% v/v sulfuric acid solution

c(BaCrO₄) = 7.5 g/L barium chromate in c(HCl) = 0.25 mol/L

c(H₂SO₄) = 25% v/v

HCl, concentrated

NH₃ solution, concentrated

Phenolphthalein indicator solution, 0.1% w/v in ethanol

c(K₂Cr₂O₇) = 0.01 mol/L standard solution, prepared from c(K₂Cr₂O₇) = 0.1 mol/L stock solution

Method:*Basic Experimental Parameters:*

Titrant delivery rate (mL/min.)	4
No. of exothermic endpoints	1
Data smoothing factor	30
ERC (2 nd derivative)	-15
Stirring speed (802 stirrer)	9
Delay before start (secs.)	60

Weigh accurately approximately 50g salt into a 400mL beaker, and equip with a magnetic stirrer follower. Stir until dissolved. While stirring, add 10 drops concentrated HCl and 10mL BaCrO₄ solution. Continue stirring for at least 20 minutes. It may take some time for the precipitate of BaSO₄ to become visible, and for all the sulfate present to react.

Add 5 drops of phenolphthalein indicator solution, and add concentrated ammonia solution until a red coloration is seen in the suspension. Filter through a dry Whatman no. 2 filter paper into a clean, dry beaker. *Note: it is important that the filtered residue in the filter paper has a pale yellow colour. This indicates the presence of BaCrO₄, which demonstrates that a satisfactory excess of BaCrO₄ has been added to the original solution. If the precipitate is white, then this indicates that insufficient BaCrO₄ has been added. The determination must be repeated, using either a smaller amount of salt or a larger volume of BaCrO₄ solution.*

Take a 50mL aliquot, add 5mL 25% v/v H₂SO₄ solution, and titrate with $c((\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}) = 0.1 \text{ mol/L}$ solution. Titrate to a single exothermic endpoint.

For low endpoint volumes (0.5mL or less), reduce the data smoothing (“filter”) factor to 15.

Standardization of $c((\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}) = 0.1 \text{ mol/L}$ titrant:

Prepare a 10mL Dosino with $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0.01 \text{ mol/L}$ solution. Prepare titration vessels with 5mL $c(\text{H}_2\text{SO}_4) = 25\% \text{ v/v}$ and 30 mL DI water. Prepare a titration program using the above parameters, but with the addition of a dosing step to dispense the K₂Cr₂O₇ solution. Conduct titrations with 1, 2, 3, 4, 5, 6 and 7mL K₂Cr₂O₇ solution. The method calculations will determine the slope and intercepts of the regression curve, the titrant molarity, and the mmol of standard K₂Cr₂O₇ solution dispensed at each aliquot. The y-intercept value shall serve as the method

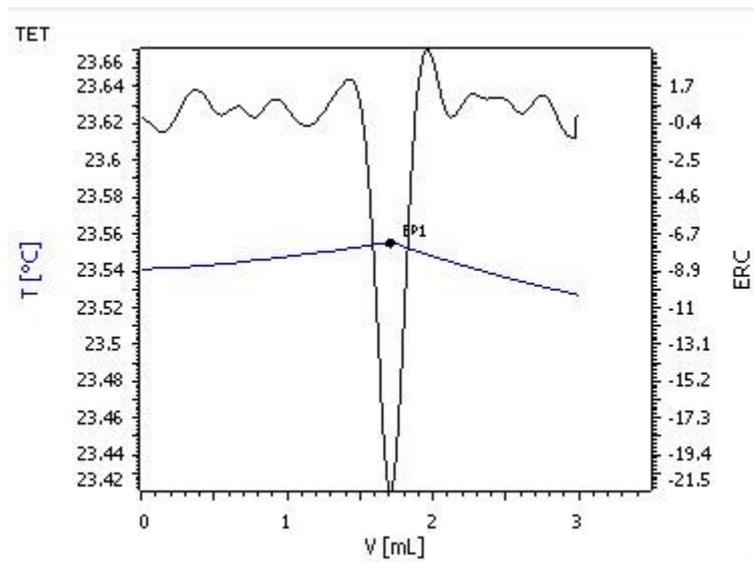
blank in this determination, and may be stored as a common variable.

Examples:	<i>Samples of rock salt (purchased from a supermarket)</i>	
	“Sea salt crystals”	0.0398±0.0002% w/w SO ₄ (n=4)
	“Lake salt”	0.0523±0.0001% w/w SO ₄ (n=4)

Calculation:
$$\text{mg/L SO}_4 = \frac{((\text{EP, mL} - \text{blank, mL}) * c(\text{Fe(II)}) * 96.0626 * 0.1)}{(\text{sample mass, g} * 3)}$$

Standardization	<i>Nominal $c((\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}) = 0.1 \text{ mol/L}$, standard = $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0.01 \text{ mol/L}$</i>
	Slope = 0.6188 Intercept = 0.0286 mL $R^2 = 1.0000$ Molarity = 0.0970 <i>(Molarity = $6 * c(\text{K}_2\text{Cr}_2\text{O}_7) / \text{slope}$)</i>

Thermometric Titration Plot:



Legend:

Blue = solution temperature curve

Black = second derivative curve