

## Titrimetric determination of sulfate

### Branch

General analytical chemistry; water, wastewater, air, environmental protection; organic chemistry, chemistry; pharmaceutical industry; food, stimulants, beverages, flavours; fertilizers, base materials, explosives; detergents, surfactants, cosmetics; mineral resources, cement

### Keywords

Sulfate; titration; potentiometric titration; photometric titration; thermometric titration; conductometric titration; Ca ISE; Pb ISE; Optrode; Thermoprobe; Tungsten Electrode; 5-ring conductivity measuring cell; DIN 53127; European Pharmacopeia; branch 1; branch 2; branch 3; branch 4; branch 7; branch 11; branch 12; branch 15; 6.0510.100; 6.1248.050; 6.0502.170; 6.1115.000; 6.9011.020; 6.0915.100

### Summary

This Bulletin describes three potentiometric, one photometric, one thermometric and one conductometric titration method for the determination of sulfate. Which indication method is the most suitable depends above all on the sample matrix.

Method 1: Precipitation as barium sulfate and back-titration of the  $\text{Ba}^{2+}$  excess with EGTA. The ion-selective calcium electrode is used as indicator electrode.

Method 2: As in method 1, but with the electrode combination tungsten/platinum.

Method 3: Precipitation titration in semi-aqueous solution with lead nitrate according to the European Pharmacopoeia using the ion-selective lead electrode as indicator electrode.

Method 4: Photometric titration with lead nitrate, dithizone indicator and the Optrode at 610 nm, particularly suitable for lower concentrations (up to 5 mg  $\text{SO}_4^{2-}$  in the sample solution).

Method 5: Thermometric precipitation titration with  $\text{Ba}^{2+}$  in aqueous solution, especially suitable for fertilizers.

Method 6: Conductometric titration with barium acetate based on DIN 53127.

## Method 1 – Ca ISE

### Summary

This method uses the cross-sensitivity of the Ca ISE for barium. A known amount of barium chloride is given to the sample, after a reaction time the remaining barium chloride is back-titrated with EGTA against the Ca ISE.

This method has the advantage that calcium present in the sample can be analyzed at the same time, while magnesium in the sample is not detected and does not interfere.

Chloride ions present in the sample do not interfere with this method if their concentration is not too high. Samples like brines or sea water must be diluted.

### Instruments

- Titrator with MET and DET mode
- 10 mL buret, 2×
- Stirrer

### Electrode

Combined polymer Ca ISE	6.0510.100
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### Reagents

- EGTA sodium salt, 98%
- Barium chloride dihydrate,  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ , 99%
- Nitric acid,  $c(\text{HNO}_3) = 1 \text{ mol/L}$
- Ammonia,  $w(\text{NH}_3) = 25\%$
- Ammonium chloride,  $\text{NH}_4\text{Cl}$
- Calcium standard, 6.2301.070
- Sodium hydroxide,  $c(\text{NaOH}) = 10 \text{ mol/L}$
- Calcium carbonate, p.a.

### Solutions

Titration	$c(\text{EGTA}) = 0.05 \text{ mol/L}$ 19.40 g EGTA sodium salt is suspended in 200 mL deionized water. While stirring $c(\text{NaOH}) = 10 \text{ mol/L}$ is added until all EGTA is dissolved. After cooling down the
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	solution is made up to 1 L with deionized water.
Barium chloride solution	$c(\text{BaCl}_2) = 0.05 \text{ mol/L}$ 12.34 g $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ is dissolved in $c(\text{HCl}) = 0.01 \text{ mol/L}$ and made up to 1000 mL with deionized water.
Buffer solution	54 g $\text{NH}_4\text{Cl}$ is weighed into a 1 L volumetric flask and dissolved in deionized water. 350 mL $w(\text{NH}_3) = 25\%$ is added and the mixture made up to 1 L with deionized water.

### Standard

$\text{CaCO}_3$	$\text{CaCO}_3$ is dried overnight in a drying oven at $105 \text{ }^\circ\text{C}$ and allowed to cool down in a desiccator for at least 1 h.
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### Sample preparation

- Samples like brines or sea water must be diluted.
- Organically bound sulfur is converted to sulfate or sulfuric acid by means of a suitable digestion procedure (e.g., Wurzschnitt digestion or Schöniger, see Appendix).

### Analysis

#### Titer

50 to 60 mg dried  $\text{CaCO}_3$  is weighed into a titration beaker and suspended in 20 mL deionized  $\text{H}_2\text{O}$ . 3 mL  $c(\text{HNO}_3) = 1 \text{ mol/L}$  is then slowly added in order to dissolve the  $\text{CaCO}_3$ . Another 30 mL deionized  $\text{H}_2\text{O}$  and 10 mL buffer solution are added to the titration beaker. The solution is then titrated with  $c(\text{EGTA}) = 0.05 \text{ mol/L}$  until after the equivalence point.

#### Blank

To 50 mL deionized water 1 mL of  $c(\text{HNO}_3) = 1 \text{ mol/L}$ , 0.5 mL calcium standard and 7.50 mL  $c(\text{BaCl}_2) = 0.05 \text{ mol/L}$  are added. After a reaction time of 3 min 5 mL buffer solution is added. The solution is then titrated with  $c(\text{EGTA}) = 0.05 \text{ mol/L}$  until after the second equivalence point.

#### Sample

A sample solution containing less than 20 mg sulfate is added to a titration beaker and diluted with 50 mL deionized water. The pH is measured and if necessary adjusted to pH 3–4 with  $c(\text{HNO}_3) = 1 \text{ mol/L}$ . 0.5 mL calcium standard (if necessary)

and 7.50 mL  $c(\text{BaCl}_2) = 0.05 \text{ mol/L}$  are added and after a reaction time of 3 min 5 mL buffer solution is added. The solution is then back-titrated with  $c(\text{EGTA}) = 0.05 \text{ mol/L}$  until after the second equivalence point.

### Parameters

#### Titer

Mode	DET U
Stirring rate	8
Pause	30 s
Signal drift	30 mV/min
Max. waiting time	32 s
Meas. point density	4
Min. increment	10 $\mu\text{L}$
Max. increment	250 $\mu\text{L}$
EP criterion	5
EP recognition	Greatest

#### Blank and Sample

Mode	MET U
Stirring rate	8
Pause	30 s
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	10 mV
EP recognition	All

### Calculation

#### Titer

$$f = \frac{m_s}{V_{EP1} \times c_{EGTA} \times M_{Std}}$$

f:	Titer of the selected titrant without unit
$m_s$ :	Mass of standard in mg
$V_{EP1}$ :	Titration consumption until the first equivalence point in mL
$c_{EGTA}$ :	Concentration of the selected titrant in mol/L; here $c(\text{EGTA}) = 0.05 \text{ mol/L}$
$M_{Std}$ :	Molecular weight of the standard in g/mol; here $M(\text{CaCO}_3) = 100.09 \text{ g/mol}$

#### Blank

$$\text{Blank} = V_{EP2} - V_{EP1}$$

Blank: Blank of the barium chloride solution in mL

$V_{EP1}$ : Titrant consumption until the first equivalence point in mL

$V_{EP2}$ : Titrant consumption until the second equivalence point in mL

### Sample

$$\beta_{SO_4} = \frac{(\text{Blank} - (V_{EP2} - V_{EP1})) \times c_{EGTA} \times f \times M_A}{V_s}$$

$\beta_{SO_4}$ : Sulfate content in g/L

Blank: Blank of the barium chloride solution in mL

$V_{EP2}$ : Titrant consumption until the second equivalence point in mL

$V_{EP1}$ : Titrant consumption until the first equivalence point in mL

$c_{EGTA}$ : Concentration of the selected titrant in mol/L; here  $c(EGTA) = 0.05 \text{ mol/L}$

f: Titer of the selected titrant without unit

$M_A$ : Molecular weight of the sulfate in g/mol; here  $96.063 \text{ g/mol}$

$V_s$ : Sample volume in mL

- If the sample contains no magnesium the expensive EGTA can be replaced by the cheaper titrant EDTA.

### Example determination

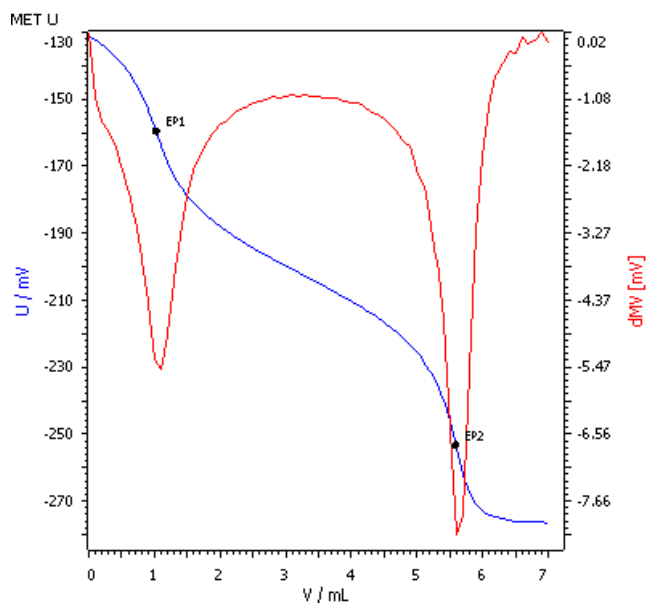


Fig. 1: Example titration curve for the determination of sulfate in an aqueous solution using the Ca ISE.

### Comments

- Calcium standard only has to be added to the sample when it does not contain any calcium.
- Calcium can be determined simultaneously. However, a high calcium content can lead to too low results of sulfate, due to the formation of gypsum ( $\text{CaSO}_4$ ).
- Magnesium is not determined, but also does not interfere with the determination.

## Method 2 – Tungsten rod electrode

### Summary

Chloride ions do not interfere with this method. Calcium, however, does interfere as it is also titrated. It therefore has to be determined separately and deducted accordingly for the sulfate titration or removed from the sample solution by means of cation exchange.

### Instruments

- Titrator with MET mode
- 10 mL buret
- Stirrer

### Electrode

Tungsten Electrode Rod with Electrode Shaft	6.1248.050 6.1241.030
Ag/AgCl Reference Electrode (KCl)	6.0726.107

### Reagents

- EGTA sodium salt, 98%
- Barium chloride dihydrate,  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ , 99%
- Hydrochloric acid,  $c(\text{HCl}) = 1 \text{ mol/L}$
- Ammonia,  $w(\text{NH}_3) = 25\%$
- Ammonium chloride,  $\text{NH}_4\text{Cl}$
- Sodium hydroxide,  $c(\text{NaOH}) = 10 \text{ mol/L}$
- Calcium carbonate, p.a.

### Solutions

Titrant	$c(\text{EGTA}) = 0.05 \text{ mol/L}$ 19.4 g EGTA sodium salt is suspended in 200 mL deionized water. While stirring $c(\text{NaOH}) = 10 \text{ mol/L}$ is added until all EGTA is dissolved. After cooling down the solution is made up to 1 L with deionized water.
Barium chloride solution	$c(\text{BaCl}_2) = 0.05 \text{ mol/L}$ 12.34 g $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ is dissolved in $c(\text{HCl}) = 0.01 \text{ mol/L}$ and made up to 1 L with deionized water.
Buffer solution	54 g $\text{NH}_4\text{Cl}$ is weighed into a 1 L volumetric flask and dissolved in

deionized water. 350 mL  $w(\text{NH}_3) = 25\%$  is added and the mixture made up to 1 L with deionized water.

### Standard

$\text{CaCO}_3$	$\text{CaCO}_3$ is dried overnight in a drying oven at $105 \text{ }^\circ\text{C}$ and allowed to cool down in a desiccator for at least 1 h.
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### Sample preparation

- To remove the calcium, percolate 50–100 mL of the aqueous sample to be analyzed through a strongly acidic cation exchanger column (e.g., Dowex 50) at a rate of 3–4 drops/s. Discard the first 5 mL. The sulfate is then determined in a portion of the treated sample solution.
- Organically bound sulfur is converted to sulfate or sulfuric acid by means of a suitable digestion procedure (e.g., Wurzschnitt digestion or Schöniger, see Appendix).

### Analysis

#### Titer

20 to 40 mg dried  $\text{CaCO}_3$  is weighed into a titration beaker and suspended in 20 mL deionized  $\text{H}_2\text{O}$ . 2 mL  $c(\text{HCl}) = 1 \text{ mol/L}$  is then slowly added in order to dissolve the  $\text{CaCO}_3$ . Another 30 mL deionized  $\text{H}_2\text{O}$  and 10 mL buffer solution are added to the titration beaker. The solution is then titrated with  $c(\text{EGTA}) = 0.05 \text{ mol/L}$  until after the equivalence point.

#### Blank

To 50 mL deionized water 1 mL of  $c(\text{HCl}) = 1 \text{ mol/L}$  and 7.50 mL  $c(\text{BaCl}_2) = 0.05 \text{ mol/L}$  are added. After a reaction time of 3 min, 5 mL buffer solution is added. The solution is then titrated with  $c(\text{EGTA}) = 0.05 \text{ mol/L}$  until after the equivalence point.

#### Sample

A sample solution containing less than 20 mg sulfate is diluted with 50 mL deionized water. The pH is measured and if necessary adjusted to pH 3–4 with  $c(\text{HCl}) = 1 \text{ mol/L}$ . 7.50 mL  $c(\text{BaCl}_2) = 0.05 \text{ mol/L}$  is added and after a reaction time of 3 min 5 mL buffer solution is added. The solution is then back-titrated with  $c(\text{EGTA}) = 0.05 \text{ mol/L}$  until after the equivalence point.

## Parameters

### Titer

Mode	MET U
Stirring rate	8
Pause	30 s
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	30 mV
EP recognition	Greatest

### Blank and Sample

Mode	MET U
Stirring rate	8
Pause	30 s
Signal drift	50 mV/min
Min. waiting time	10 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	20 mV
EP recognition	Greatest

## Calculation

### Titer

$$f = \frac{m_s}{V_{EP1} \times c_{EGTA} \times M_{Std}}$$

- f: Titer of the selected titrant without unit  
 m<sub>s</sub>: Mass of standard in mg  
 V<sub>EP1</sub>: Titrant consumption until the first equivalence point in mL  
 c<sub>EGTA</sub>: Concentration of the selected titrant in mol/L; here c(EGTA) = 0.05 mol/L  
 M<sub>Std</sub>: Molecular weight of the standard in g/mol; here M(CaCO<sub>3</sub>) = 100.09 g/mol

### Blank

$$\text{Blank} = V_{EP1}$$

- Blank: Blank of the barium chloride solution in mL  
 V<sub>EP1</sub>: Titrant consumption until the first equivalence point in mL

## Sample

$$\beta_{SO_4} = \frac{(\text{Blank} - V_{EP1}) \times c_{EGTA} \times f \times M_A}{V_s}$$

- β<sub>SO<sub>4</sub></sub>: Content of sulfate in g/L  
 Blank: Blank of the barium chloride solution in mL  
 V<sub>EP1</sub>: Titrant consumption until the first equivalence point in mL  
 c<sub>EGTA</sub>: Concentration of the selected titrant in mol/L; here c(EGTA) = 0.05 mol/L  
 f: Titer of the selected titrant without unit  
 M<sub>A</sub>: Molecular weight of the sulfate in g/mol; here 96.063 g/mol  
 V<sub>s</sub>: Sample volume in mL

## Example determination

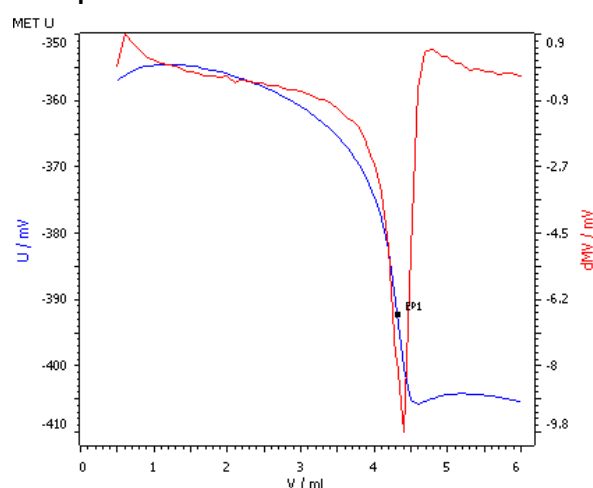


Fig. 2: Example titration curve for the determination of sulfate in an aqueous solution using the tungsten electrode.

## Comments

- For the titer determination the cross-sensitivity of the electrode for calcium is utilized.
- The sample solution has to be acidified to pH < 4 with hydrochloric acid before adding BaCl<sub>2</sub>.

## Method 3 – Pb ISE

### Summary

Phosphate and calcium interfere with this titration and must therefore be absent. Chloride, hydrogen carbonate and carbonate ions interfere with this method if their concentration is 50 times higher than the sulfate concentration.

The sample should contain no acetate ions as these can severely affect the response of the ion-selective lead electrode.

### Instruments

- Titrator with DET mode
- 10 mL buret
- Stirrer

### Electrode

Ion-selective electrode Pb	6.0502.170
LL ISE Reference	6.0750.100

### Reagents

- Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$
- Methanol
- Hydrochloric acid,  $c(\text{HCl}) = 0.1 \text{ mol/L}$
- Sodium hydroxide,  $c(\text{NaOH}) = 0.05 \text{ mol/L}$
- Sulfuric acid conc.

### Solutions

Titratant	$c(\text{Pb}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$ Approx. 33.1 g $\text{Pb}(\text{NO}_3)_2$ is weighed into a 1 L volumetric flask and dissolved in deion. $\text{H}_2\text{O}$ . The flask is then filled up to the mark with deion. $\text{H}_2\text{O}$ .
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### Standard

TRIS	TRIS is dried over night in a drying oven at $105 \text{ }^\circ\text{C}$ and allowed to cool down in a desiccator for at least 1 h.
Sulfuric acid	$c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$ If possible this solution should be bought from supplier.

### Sample preparation

- In aqueous samples the chloride is titrated with silver nitrate using the 6.0430.100 Ag Titrode. Percolate the titrated sample through a strongly acidic cation exchanger column and make up to 50 mL by rinsing with dist. water (do not discard the initial drops). 10 mL of the sample solution thus treated is then used for the sulfate titration.
- Organically bound sulfur is converted to sulfate or sulfuric acid by means of a suitable digestion procedure (e.g., Wurzschnitt digestion or Schöniger, see Appendix).

### Analysis

#### Titer $\text{H}_2\text{SO}_4$

70 to 90 mg dried TRIS is weighed into a titration beaker and dissolved in 50 mL deionized  $\text{H}_2\text{O}$ . The solution then is titrated with  $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$  until after the equivalence point.

#### Titer $\text{Pb}(\text{NO}_3)_2$

5 mL  $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$  is pipetted into a titration beaker containing 20 mL deionized  $\text{H}_2\text{O}$ . After the addition of 5 mL  $c(\text{NaOH}) = 0.05 \text{ mol/L}$  and 40 mL methanol the solution is titrated with  $c(\text{Pb}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$  until after the equivalence point.

#### Sample

An appropriate amount of sample is weighed into a titration beaker and dissolved in 20 mL deionized  $\text{H}_2\text{O}$  and 0.1 mL  $c(\text{HCl}) = 0.1 \text{ mol/L}$ . After dissolution 40 mL methanol is added to the titration beaker. The solution is then titrated with  $c(\text{Pb}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$  until after the equivalence point.

### Parameters

For all titrations the same parameters were used.

Mode	DET U
Stirring rate	8
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 $\mu\text{L}$
EP criterion	5
EP recognition	Greatest

## Calculation

### Titer $H_2SO_4$

$$f_{H_2SO_4} = \frac{m_s}{V_{EP1} \times c_{H_2SO_4} \times M_S \times 2}$$

$f_{H_2SO_4}$ :	Titer of $c(H_2SO_4) = 0.05$ mol/L without unit
ms:	Sample size in mg
$V_{EP1}$ :	Titrant consumption until the first equivalence point in mL
$c_{H_2SO_4}$ :	Concentration of the selected titrant in mol/L; here $c(H_2SO_4) = 0.05$ mol/L
Ms:	Molecular weight of the standard in g/mol; here $M(TRIS) = 121.14$ g/mol
2:	Stoichiometric factor

### Titer $Pb(NO_3)_2$

$$f_{Pb(NO_3)_2} = \frac{V_S \times c_{H_2SO_4} \times f_{H_2SO_4}}{V_{EP1} \times c_{Pb(NO_3)_2}}$$

$f_{Pb(NO_3)_2}$ :	Titer of $c(Pb(NO_3)_2) = 0.1$ mol/L without unit
$V_{EP1}$ :	Titrant consumption until the first equivalence point in mL
$c_{H_2SO_4}$ :	Concentration of the standardized sulfuric acid in mol/L; here $c(H_2SO_4) = 0.05$ mol/L
$f_{H_2SO_4}$ :	Titer of the standardized sulfuric acid without unit
$V_S$ :	Added volume of the standardized sulfuric acid in mL
$c_{Pb(NO_3)_2}$ :	Concentration of the selected titrant in mol/L; here $c(Pb(NO_3)_2) = 0.1$ mol/L

### Sample

$$w_{SO_4} = \frac{V_{EP1} \times c_{Pb(NO_3)_2} \times f_{Pb(NO_3)_2} \times M_A}{m_s} \times 100$$

$w_{SO_4}$ :	Content of sulfate in g/L
$V_{EP1}$ :	Titrant consumption until the first equivalence point in mL
$c_{Pb(NO_3)_2}$ :	Concentration of the selected titrant in mol/L; here $c(Pb(NO_3)_2) = 0.1$ mol/L
$f_{Pb(NO_3)_2}$ :	Titer of the selected titrant without unit
$M_A$ :	Molecular weight of the $SO_4$ in g/mol; here 96.063 g/mol
ms:	Sample size in mg
100:	Conversion factor

## Example determination

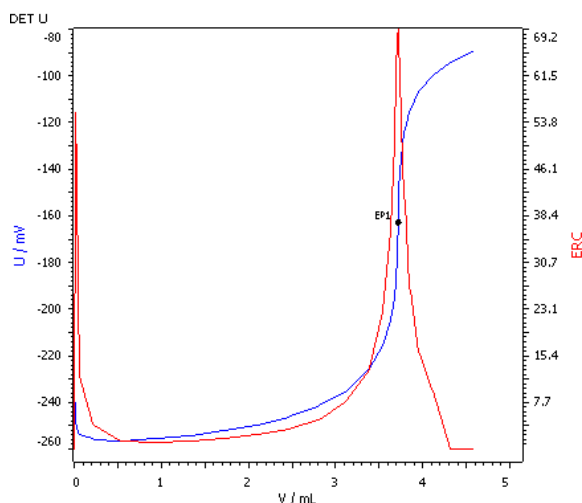


Fig. 3: Example titration curve for the determination of sulfate in anhydrous sodium sulfate using the Pb ISE.

## Comments

- The surface of the Pb ISE has to be polished when the potential jump becomes flatter. For this the Metrohm polishing set for solid-state electrodes (6.2802.000) has to be used.
- The addition of NaOH in the titer determination of lead nitrate is necessary as without it no potential jump is obtained.
- The samples have to be titrated in a slight acidic environment, as otherwise carbonate interferes. This is not necessary for the titer determination as there sulfuric acid is used for the standardization.
- Instead of methanol other alcohols e.g., 2-propanol can be used.

## References

- European Pharmacopeia  
Sodium sulfate anhydrous
- European Pharmacopeia  
Sodium sulfate decahydrate
- DIN EN 14880  
Surface active agents - Determination of inorganic sulphate content in anionic surface active agents - Potentiometric lead selective electrode titration method
- J.O. Goertzen, J.D. Oster, Potentiometric titration of sulfate in water and soil extracts using a lead electrode, Soil. Sci. Soc. Am. J., 36, (1972), 691-693.
- E.P. Scheide, R.A. Durst, Indirect determination of sulfate in natural water by ion-selective electrode, Anal. Lett., 10, (1977), 55-56.

## Method 4 – Optrode

### Summary

As this is a precipitation titration with photometric endpoint indication, only lower concentrations (up to 10 mg SO<sub>4</sub><sup>2-</sup> in the sample) should be carried out. Higher sulfate contents will cause interferences due to precipitation. Lead perchlorate should not be used as titrant because then chloride ions would interfere with this method.

### Instruments

- Titrator with SET and MET mode
- 10 mL buret
- Stirrer

### Electrode

Optrode (610 nm)	6.1115.000
Unitrode easyClean with Pt1000	6.0260.010

### Reagents

- Lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>
- Acetone
- Nitric acid, c(HNO<sub>3</sub>) = 1 mol/L
- Dithizone
- Sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>

### Solutions

Titrant	c(Pb(NO <sub>3</sub> ) <sub>2</sub> ) = 0.01 mol/L Approx. 3.3 g Pb(NO <sub>3</sub> ) <sub>2</sub> is weighed into a 1 L volumetric flask and dissolved in deion. H <sub>2</sub> O. The flask is then filled up to the mark with deion. H <sub>2</sub> O.
Indicator solution	50 mg dithizone is dissolved in 100 mL acetone.

### Standard solution

Na <sub>2</sub> SO <sub>4</sub> standard solution	Na <sub>2</sub> SO <sub>4</sub> is dried over night in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. 142 mg dried Na <sub>2</sub> SO <sub>4</sub> is weighed into a 100 mL volumetric flask and dissolved in deion. H <sub>2</sub> O. The flask is then filled up to the mark with deion. H <sub>2</sub> O.
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### Sample preparation

- Organically bound sulfur is converted to sulfate or sulfuric acid by means of a suitable digestion procedure (e.g., Wurzschnitt digestion or Schöniger, see Appendix).

### Analysis

#### Blank

5 mL deion. H<sub>2</sub>O and 0.4 mL dithizone indicator solution are pipetted into a titration beaker. After the addition of 50 mL acetone the pH value is adjusted to pH 2 using a SET titration with c(HNO<sub>3</sub>) = 1 mol/L. The solution is then immediately titrated with Pb(NO<sub>3</sub>)<sub>2</sub> = 0.01 mol/L until after the equivalence point.

#### Titer

1.5 mL sodium sulfate standard solution and 0.4 mL dithizone indicator solution are pipetted into a titration beaker and deion. H<sub>2</sub>O is added to obtain a sample volume of 5 mL. After the addition of 50 mL acetone the pH value is adjusted to pH 2 using a SET titration with c(HNO<sub>3</sub>) = 1 mol/L. The solution is then immediately titrated with Pb(NO<sub>3</sub>)<sub>2</sub> = 0.01 mol/L until after the equivalence point.

#### Sample

The sample, containing not more than 10 mg SO<sub>4</sub><sup>2-</sup>, and 0.4 mL dithizone indicator solution are pipetted into a titration beaker and deion. H<sub>2</sub>O is added to obtain a total 5 mL sample volume of 5 mL. After the addition of 50 mL acetone the pH value is, if necessary, adjusted to pH 2 using a SET titration with c(HNO<sub>3</sub>) = 1 mol/L. The solution is then immediately titrated with Pb(NO<sub>3</sub>)<sub>2</sub> = 0.01 mol/L until after the equivalence point.



## Parameters

### SET pH

Stirring rate	8
EP1 at pH	2
Titration rate	Slow
Stop criterion	Drift
Stop drift	20 $\mu$ L/min

### Blank, Titer and Sample

Mode	MET U
Stirring rate	8
Start volume	0 mL
Pause	30 s
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	0.05 mL
EP criterion	20 mV
EP recognition	Greatest

## Calculation

### Blank

$$\text{Blank} = V_{\text{EP1}}$$

Blank: Blank in mL

$V_{\text{EP1}}$ : Titrant consumption until the first equivalence point in mL

### Titer

$$f = \frac{V_S \times \beta_S}{(V_{\text{EP1}} - \text{Blank}) \times c_{\text{Pb}(\text{NO}_3)_2} \times M_S}$$

Titer: Titer of the selected titrant without unit

$V_S$ : Volume of standard solution in mL

$\beta_S$ : Exact mass concentration of standard in g/L

Blank: Blank in mL

$V_{\text{EP1}}$ : Titrant consumption until the first equivalence point in mL

$c_{\text{Pb}(\text{NO}_3)_2}$ : Concentration of the selected titrant in mol/L; here  $c(\text{Pb}(\text{NO}_3)_2) = 0.01$  mol/L

$M_S$ : Molecular weight of the standard in g/mol; here  $c(\text{Na}_2\text{SO}_4) = 142.04$  g/mol

## Sample

$$\beta_{\text{SO}_4} = \frac{(V_{\text{EP1}} - \text{Blank}) \times c_{\text{Pb}(\text{NO}_3)_2} \times f \times M_A}{V_S}$$

$\beta_{\text{SO}_4}$ : Content of sulfate in g/L

Blank: Blank in mL

$V_{\text{EP1}}$ : Titrant consumption until the first equivalence point in mL

$c_{\text{Pb}(\text{NO}_3)_2}$ : Concentration of the selected titrant in mol/L; here  $c(\text{Pb}(\text{NO}_3)_2) = 0.01$  mol/L

f: Titer of the selected titrant without unit

$M_A$ : Molecular weight of the sulfate in g/mol; here 96.063 g/mol

$V_S$ : Sample volume in mL

## Example determination

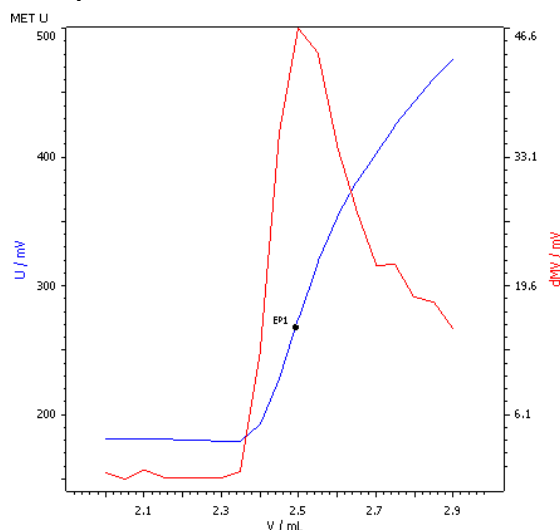


Fig. 4: Example titration curve for the determination of sulfate in diluted sulfuric acid using the Optrode.

## Comments

- If the pH for the titration with dithizone is below pH 1, a precipitation occurs in the solution, resulting in v-shaped titration curves. Therefore acidic samples should be adjusted to a pH of 2.
- Heavy metal cations which form colored complexes with dithizone (e.g.,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ) interfere with the titration and must be removed using an ion-exchange resin.
- Phosphates also interfere with the titration. They can be removed by precipitation with magnesium carbonate followed by cold filtration (10 °C).

**References**

- IP 242/83  
Sulfur in petroleum products – flask combustion method.
- P. Borda, Determination of sulfur in organometallic compounds by the oxygen flask method, *Anal. Chim. Acta*, 196 (1987), 355–357.
- Fritz; J.S. Yamamura; S.S, Rapid microtitration of sulfate, *Anal. Chem.*, 27, 1955, 9, 1461 - 1464.
- White; D.C., The titrimetric microdetermination of sulphate using lead nitrate as titrant and dithizone as indicator, *Mikrochimica Acta*, 47, 1958, 2, 254-269.
- Hwang; H, Dasgupta; P.K, Microtitration of sulfate with beryllon II as indicator: determination of sulfate in environmental samples, *Mikrochimica Acta*, 1984, 2, 159-168.
- ISO 6844:1983  
Surface active agents – Determination of mineral sulfate content – Titrimetric method.

## Method 5 – Titrotherm

### Summary

The thermometric titration of sulfate with barium chloride is a fast alternative to the potentiometric titrations. It is in particular suitable for fertilizers (liquid or granular) for which the determination is described here.

### Instruments

- 859 Titrotherm
- 5 mL buret
- Rod stirrer

### Electrode

Thermoprobe	6.9011.020
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### Reagents

- Barium chloride, BaCl<sub>2</sub>
- Hydrochloric acid, HCl, conc.
- Nitric acid, c(HNO<sub>3</sub>) = 5 mol/L
- Sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>

### Solutions

Titrant	c(BaCl <sub>2</sub> ) = 1 mol/L
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### Standard

Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub> is dried at 105 °C in a drying oven for 2 h and cooled down in a desiccator for at least 1 h.
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### Sample preparation

- For liquid fertilizers no sample preparation is necessary.
- Granular fertilizers are first dissolved in conc. HCl. An appropriate sample size (see comments) is weighed out into a titration vessel. For each g sample 1 mL conc. HCl is added. The titration vessel is placed on a moderately heated hot plate and the sample is heated and stirred until it is dissolved.  
In order to avoid loss of sample the titration vessel can be covered with a short stem funnel. Droplets adherent to the funnel can be rinsed off into the titration vessel after dissolution.

### Analysis

#### Titer

Titrate at least 4 different aliquots of the sample in an ascending order.

100–600 mg dried Na<sub>2</sub>SO<sub>4</sub> is weighed accurately into a titration vessel. 1 mL c(HNO<sub>3</sub>) = 5 mol/L and 30 mL deionized water are added. The solution is then titrated with c(BaCl<sub>2</sub>) = 1 mol/L until after the exothermic endpoint.

#### Blank

Titrate at least 4 different aliquots of the sample in an ascending order.

An appropriate amount of sample is weighed accurately into a titration vessel. If necessary 1 mL c(HNO<sub>3</sub>) = 5 mol/L is added to acidify the sample. Then 30 mL deionized water is added and the solution is titrated with c(BaCl<sub>2</sub>) = 1 mol/L until after the exothermic endpoint..

#### Sample

An appropriate amount of sample is weighed accurately into a titration vessel. If necessary 1 mL c(HNO<sub>3</sub>) = 5 mol/L is added to acidify the sample. 30 mL deionized water is added and the solution is then titrated with c(BaCl<sub>2</sub>) = 1 mol/L until after the exothermic endpoint..

### Parameters

#### Titer

Stirring rate	6
Pause	10 s
Dosing rate	6 mL/min
Filter factor	60
Damping until	0.5 mL
Evaluation start	0.5 mL
Reaction type	Exothermic
EP criterion	-20

#### Blank/Sample

Stirring rate	8
Pause	20 s
Dosing rate	6 mL/min
Filter factor	50
Damping until	0.5 mL
Evaluation start	0.5 mL
Reaction type	Exothermic
EP criterion	-20

## Calculation

For more details on the calculation of the titer and the blank in *tiamo*<sup>TM</sup> please refer to the Application Note H-131.

### Titer

A linear regression of the consumed titrant volume in mL versus the different volumes of standard in mg is evaluated by *tiamo*<sup>TM</sup>. The titer is calculated from the slope.

$$f = \frac{1}{a \times M_{\text{Std}} \times c_{\text{BaCl}_2}}$$

f:	Titer of the titrant without unit
a:	Slope of the linear regression in mL/mg
M <sub>Std</sub> :	Molecular weight of the standard in g/mol; here (Na <sub>2</sub> SO <sub>4</sub> ) = 142.042 g/mol
c <sub>BaCl<sub>2</sub></sub> :	Concentration of the selected titrant in mol/L; here c(BaCl <sub>2</sub> ) = 1 mol/L

### Blank

A linear regression of the different sample volumes (mL) against the volume (mL) of titrant consumed is evaluated by *tiamo*<sup>TM</sup>. The method blank is defined as the intercept of the linear regression line with the y-axis.

### Sample

$$w_{\text{SO}_4} = \frac{(V_{\text{EP1}} - \text{Blank}) \times c_{\text{BaCl}_2} \times f \times M_{\text{A}} \times 0.1}{m_{\text{S}}}$$

w <sub>SO<sub>4</sub></sub> :	Sulfate content in %
V <sub>EP1</sub> :	Titration consumption until the exothermic endpoint in mL
Blank:	Method blank in mL
c <sub>BaCl<sub>2</sub></sub> :	Concentration of the selected titrant in mol/L; here c(BaCl <sub>2</sub> ) = 1 mol/L
f:	Titer of BaCl <sub>2</sub>
M <sub>A</sub> :	Molecular weight of sulfate in g/mol; 96.063 g/mol
0.1:	Conversion factor to obtain the result in %
m <sub>S</sub> :	Sample size in g

## Example determination

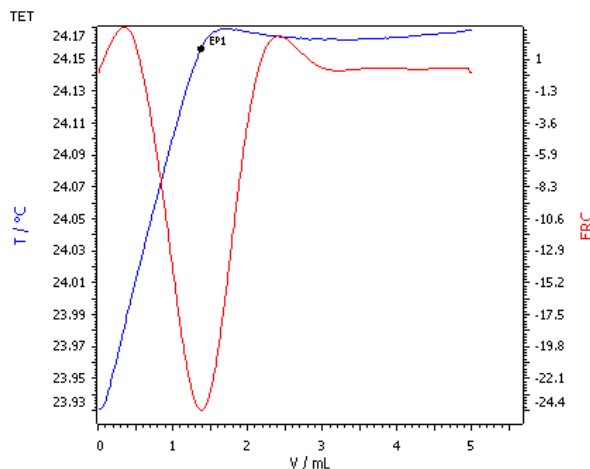


Fig. 5: Thermometric titration curve of the sulfate determination in liquid fertilizer.

## Comments

- The Thermoprobe should not be left within the titrated solution as barium sulfate precipitates on it. This can lead to serious measuring problems. If a Thermoprobe is coated with barium sulfate it can be cleaned by immersion into conc. sulfuric acid for 2 min while stirring. Afterwards the Thermoprobe is immersed into deion. water for 2 min while stirring to rinse of the remaining sulfuric acid.
- The sample size should be chosen in such a way as to obtain an endpoint between 1 and 2 mL.
- The nitric acid is added in order to ensure that the sample solution is acidic. For acidic samples this can be omitted.
- The sample size for the sample determination should be within the linear range of the blank determination.
- For granular fertilizer the pause before the titration has to be increased for full dissolution (see also AB 307).

## References

- Application Bulletin 307  
Determination of sulfate in granular phosphate fertilizers with 859 Titrotherm
- Application Bulletin 308  
Determination of sulfate in phosphoric acid (liquid fertilizer samples) with 859 Titrotherm
- Application Note H-131  
Determination of titer and method blank for thermometric titrations using *tiamo*<sup>TM</sup>

## Method 6 – Conductometry

### Summary

The conductometric titration of sulfate with barium acetate is for example applied for the determination of sulfate in paper and board.

### Instruments

- Conductivity meter
- 10 mL buret
- Rod stirrer
- Titration vessel with thermostat jacket
- Thermostat

### Electrode

5-ring conductivity cell,  $c = 0.7 \text{ cm}^{-1}$  with Pt1000 6.0915.100

### Reagents

- Barium acetate,  $\text{Ba}(\text{CH}_3\text{COO})_2$ , p.a.
- Acetone, p.a.
- Sodium sulfate,  $\text{Na}_2\text{SO}_4$

### Solutions

**Titration**  $c(\text{Ba}(\text{CH}_3\text{COO})_2) = 0.1 \text{ mol/L}$   
 Approx. 25.5 g  $\text{Ba}(\text{CH}_3\text{COO})_2$  is weighed into a 1 L volumetric flask and dissolved in deion.  $\text{H}_2\text{O}$ . The flask is then filled up to the mark with deion.  $\text{H}_2\text{O}$ .

**Solvent** Acetone

### Standard

**$\text{Na}_2\text{SO}_4$**   $\text{Na}_2\text{SO}_4$  is dried at  $105 \text{ }^\circ\text{C}$  in a drying oven for 2 h and cooled down in a desiccator for at least 1 h.

### Sample preparation

The sample preparation for paper and board samples is done as described in the norm.

### Analysis

#### Titer

50–100 mg dried  $\text{Na}_2\text{SO}_4$  is weighed accurately into a titration vessel. 50 mL acetone and 50 mL deion  $\text{H}_2\text{O}$  are added and the temperature is set to  $25 \pm 0.2 \text{ }^\circ\text{C}$ . Afterwards the solution is titrated with  $c(\text{Ba}(\text{CH}_3\text{COO})_2) = 0.1 \text{ mol/L}$  until after the equivalence point.

#### Sample

50 mL sample solution is pipetted into the titration vessel and 25–50 mL acetone is added. After a stable temperature of  $25 \pm 0.2 \text{ }^\circ\text{C}$  is reached the solution is titrated with  $c(\text{Ba}(\text{CH}_3\text{COO})_2) = 0.1 \text{ mol/L}$  until after the equivalence point.

### Parameters

#### Titer

Mode	MET Cond
Stirring rate	8
Signal drift	0.1 (mS/cm)/min
Max. waiting time	28 s
Volume increment	0.1 mL
Evaluation	Without window
Smoothing	20

#### Sample

Mode	MET Cond
Stirring rate	8
Signal drift	0.1 (mS/cm)/min
Max. waiting time	28 s
Volume increment	0.1 mL
Evaluation	Without window
Smoothing	20

### Calculation

#### Titer

$$f = \frac{m_s}{V_{EP1} \times c_{\text{Ba}(\text{CH}_3\text{COO})_2} \times M_{\text{Std}}}$$

- f: Titer of the selected titrant without unit  
 $m_s$ : Mass of standard in mg  
 $V_{EP1}$ : Titration consumption until the first equivalence point in mL  
 $c_{\text{EGTA}}$ : Concentration of the selected titrant in mol/L; here  $c(\text{Ba}(\text{CH}_3\text{COO})_2) = 0.1 \text{ mol/L}$   
 $M_{\text{Std}}$ : Molecular weight of the standard; here  $M(\text{Na}_2\text{SO}_4) = 142.04 \text{ g/mol}$

**Sample**

$$w_{\text{SO}_4} = \frac{V_{\text{EP1}} \times c_{\text{Ba}(\text{CH}_3\text{COO})_2} \times f \times M_{\text{A}} \times 0.1}{m_{\text{S}}}$$

- $w_{\text{SO}_4}$ : Sulfate content in %  
 $V_{\text{EP1}}$ : Titrant consumption until the first equivalence point in mL  
 $c_{\text{Ba}(\text{CH}_3\text{COO})_2}$ : Concentration of the selected titrant in mol/L;  
 here  $c(\text{Ba}(\text{CH}_3\text{COO})_2) = 0.1 \text{ mol/L}$   
 $f$ : Titer of the selected titrant without unit  
 $M_{\text{A}}$ : Molecular weight of sulfate in g/mol;  
 96.063 g/mol  
 0.1: Conversion factor to obtain the result in %  
 $m_{\text{S}}$ : Sample size in g

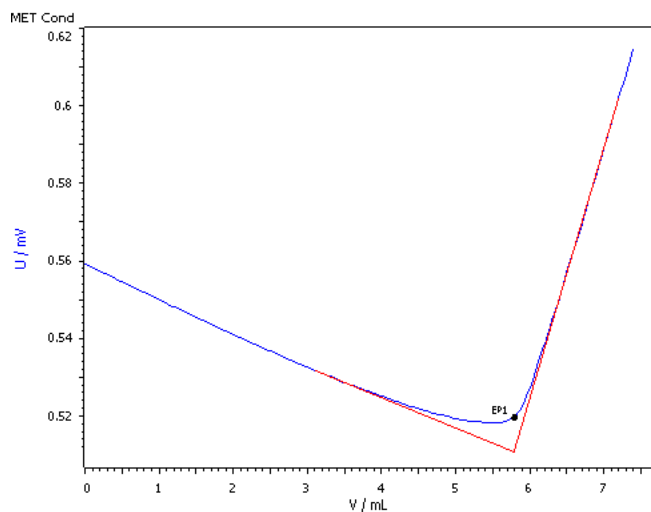
**Example determination**


Fig. 6: Titration curve of sodium sulfate.

**Comments**

- The amount of acetone added depends on the sample matrix.

**References**

- DIN 53127:2004  
 Testing of paper and board - Determination of water-soluble sulfates in paper and board

**Author**

Competence Center Titration  
 Metrohm International Headquarters

## Appendix

The appendix contains information on different digestion methods. These are only example methods, other digestion methods may be applied as sample preparation.

### Schöniger combustion

10–30 mg sample is weighed exactly onto a sulfate-free filter paper (shape according to DIN 51400) and distributed evenly. Fit the filter paper into the platinum gauze cage of the ignition device.

Pour 20 mL  $w(\text{H}_2\text{O}_2) = 10\%$  into a 500 mL digestion flask, then fill the remaining space in the flask with pure oxygen. Fit the ignition device into the mouth of the digestion flask and ignite the sample. When combustion is finished, keep the flask closed and shake until the smoke has been completely absorbed by the liquid. Rinse out the liquid into a glass beaker with dist. water, add 1 mL  $c(\text{NaOH}) = 0.1 \text{ mol/L}$  and evaporate to dryness. Take care also to heat the walls of the glass beaker, since residual peroxide can interfere with the sulfate determination. Dissolve the residue in 10 mL dist. water, then titrate the sulfate.

### Wurzschnitt digestion

To avoid accidents, please adhere strictly to the instructions for use for the digestion apparatus!

We have treated an organic substance ( $M = 500 \text{ g/mol}$ , 1 S atom) as follows:

250 g sample is digested in the Wurzschnitt bomb with 250 mg ethylene glycol and 12 g sodium peroxide. After cooling down, the residue is dissolved in approx. 100 mL dist. water, boiled and allowed to cool down again. The solution is then neutralized with conc.  $\text{HNO}_3$  and made up to 250 mL with dist. water in a volumetric flask at 20 °C. 1–10 mL of this sample solution is then used for the sulfate titration. Using a sample weight of 500 mg the limit of quantitation is 0.008% S.