
Application Bulletin

Of interest to: General analytical laboratories

A C 1, 2, 3, 7, 11, 12, 15

Titrimetric determination of sulfate

Summary

The present bulletin describes three potentiometric and one photometric titration method for the determination of sulfate. Which indication method is the most suitable depends above all on the sample matrix and is illustrated with examples in this bulletin.

Method 1: Precipitation as barium sulfate and back-titration of the Ba²⁺ 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 perchlorate using the ion-selective lead electrode as indicator electrode.

Method 4: Photometric titration with barium perchlorate, thorin indicator and the 662 Photometer or 525 nm Spectrode. Particularly suitable for micro determinations!

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.223 Exchange unit(s)

The necessary electrodes and other accessories are listed under the different methods.

Sample preparation

A) If calcium and magnesium ions interfere (method 2)

Sample matrix: mostly water samples

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 sample solution thus treated.

B) If chloride ions interfere (method 3)

In the aqueous sample 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.

C) Organically bound sulfur

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

Examples:

Combustion according to Schöniger

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. Neutralize with conc. HNO_3 and make 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.

Method 1**General**

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. Calcium can be determined simultaneously. If no calcium ions are present, they can be added to the sample prior to the titration. Magnesium is not determined, but also does not interfere with the determination.

Electrodes

- 6.0504.100 ion-selective calcium electrode (Ca ISE) with 6.2104.020 electrode cable
- 6.0726.107 double-junction Ag/AgCl reference electrode [filled with c(KCl) = 3 mol/L] with 6.2106.020 electrode cable

Reagents

- Barium chloride solution, c(BaCl₂) = 0.05 mol/L:
Dissolve 12.34 g BaCl₂ * 2 H₂O (99%) in c(HCl) = 0.1 mol/L and make up to 1 L.
- Titrant: c(EGTA) = 0.05 mol/L:
Make a suspension with 19.4 g ethylene glycol-bis-(2-aminoethyl)-tetraacetic acid (98%) and 200 mL dist. water. Under stirring add c(NaOH) = 10 mol/L until everything has dissolved. Allow to cool down and make up to 1 L with dist. water.
- Ca²⁺ standard solution, c(CaCl₂) = 0.1 mol/L, e.g. Metrohm no. 6.2301.070
- Buffer solution pH = 10:
Dissolve 9 g NH₄Cl and 60 mL w(NH₃) = 25% in dist. water and make up to 1 L.

Analysis

Acidify the sample solution, if required, to pH <4 with hydrochloric acid and add a defined volume (excess) of c(BaCl₂) = 0.05 mol/L. If necessary, add 0.5 mL c(CaCl₂) = 0.1 mol/L and allow to react for 3 min under stirring. Afterwards add 5 mL buffer solution pH = 10 and allow to react for another 30 s, then titrate with c(EGTA) = 0.05 mol/L.

Two equivalence points are obtained, the first of which corresponds to the Ca²⁺ content and the difference between the second and the first equivalence point to the Ba²⁺ excess.

The titrant consumption for the added quantity of c(BaCl₂) = 0.05 mol/L has first to be determined. This is done by means of a blank sample (without sulfate), which is prepared and titrated in exactly the same way as the actual sample. The resulting blank consumption is stored as common variable C30 in the titrator.

Calculation

1 mL c(EGTA) = 0.05 mol/L corresponds to 4.803 mg SO₄²⁻ or 1.603 mg S
2.004 mg Ca²⁺

$$RS1 = \text{mg/L Ca}^{2+} = EP1 * C01 * C02 / C00$$

$$RS2 = EP2 - EP1; \text{ mL}$$

$$RS3 = \text{mg/L SO}_4^{2-} = (C30 - RS2) * C03 * C02 / C00$$

$$EP1 = \text{titrant consumption to reach the first EP in mL}$$

$$EP2 = \text{titrant consumption to reach t EP in mL}$$

$$C00 = \text{sample volume in mL}$$

$$C01 = 2.004$$

$$C02 = 1000 \text{ (conversion factor in mL/L)}$$

$$C03 = 4.803$$

$$C30 = \text{blank consumption in mL [use the same quantity of c(BaCl}_2\text{) = 0.05 mol/L for the blank as for the sample!]}$$

Remarks

- Alkaline sample solutions have to be acidified to pH <4 with hydrochloric acid before adding BaCl₂.
- If the sample contains no magnesium the expensive EGTA can be replaced by the cheaper titrant EDTA.

Method 2**General**

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 in the sulfate titration or removed from the sample solution by means of cation exchange.

Electrodes

- 6.1248.050 W electrode rod with 6.1241.030 electrode shaft and 6.2114.000 electrode cable
- 6.1248.000 Pt electrode rod with 6.1241.030 electrode shaft and 6.2106.020 electrode cable or
6.0726.107 double-junction Ag/AgCl reference Electrode [filled with c(KCl) = 3 mol/L] with 6.2106.020 electrode cable

Reagents

As described under method 1, except for the Ca²⁺ standard solution.

Analysis

Acidify the sample solution to pH <4 with hydrochloric acid and add a defined volume (excess) of c(BaCl₂) = 0.05 mol/L. Allow to react for 3 min under stirring. Afterwards add 5 ... 10 mL buffer solution pH = 10 and titrate back the Ba²⁺ excess with c(EGTA) = 0.05 mol/L using the MET mode (volume increment: 0.1 mL, fixed waiting time: 20 s).

The titrant consumption for the added quantity of c(BaCl₂) = 0.05 mol/L has first to be determined. This is done by means of a blank sample (without sulfate), which is prepared and titrated in exactly the same way as the actual sample. The resulting blank consumption is stored as common variable C30 in the titrator.

Calculation

1 mL c(EGTA) = 0.05 mol/L corresponds to 4.803 mg SO₄²⁻ or 1.603 mg S

$$\text{mg/L SO}_4^{2-} = (\text{C30} - \text{EP1}) * \text{C01} * \text{C02} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = sample volume in mL

C01 = 4.803

C02 = 1000 (conversion factor in mL/L)

C30 = blank consumption in mL

Remarks

- The sample solution has to be acidified to pH <4 with hydrochloric acid before adding BaCl₂.
 - For the blank the same quantity of c(BaCl₂) = 0.05 mol/L has to be used as for the sample.
 - With the Pt electrode steeper and better titration curves are obtained than with the Ag/AgCl reference electrode.
-

Method 3**General**

Chloride, hydrogen carbonate and carbonate ions interfere with the determination. The sample should contain no acetate ions as these can severely affect the response of the ion-selective lead electrode.

Electrodes

- 6.0502.170 ion-selective lead electrode (Pb ISE) with 6.2104.020 electrode cable
 - 6.0808.000 glassy carbon rod electrode with 6.2106.020 electrode cable (as reference electrode)
-

Reagents

- Titrant: lead perchlorate solution, c[Pb(ClO₄)₂] = 0.005 mol/L in φ(isopropanol) = 85% (volume fraction):
Made from Pb²⁺ standard solution c[Pb(ClO₄)₂] = 0.1 mol/L, Metrohm no. 6.2301.050
 - Perchloric acid, c(HClO₄) = 1 mol/L
 - Isopropanol, p.a.
-

Analysis

To 10.0 mL chloride-free sample solution add 70 mL isopropanol and 1 mL c(HClO₄) = 1 mol/L and titrate with c[Pb(ClO₄)₂] = 0.005 mol/L using the MET mode (volume increment: 0.1 mL, fixed waiting time: 30 s).

Calculation

1 mL c[Pb(ClO₄)₂] = 0.005 mol/L corresponds to 0.4803 mg SO₄²⁻ or 0.1603 mg S

$$\text{mg/L SO}_4^{2-} = \text{EP1} * \text{C01} * \text{C02} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = 10.0 (sample volume in mL)

C01 = 0.4803

C02 = 1000 (conversion factor in mL/L)

Remark

The surface of the Pb ISE has to be polished from time to time with moist aluminum oxide powder (6.2802.000 polishing set).

Method 4**General**

As this is a precipitation titration with photometric endpoint indication, only micro-determinations should be carried out. (Greater sulfate contents will cause interferences due to precipitation, which also occurs on the mirror of the light guide.) Lead perchlorate should not be used as titrant because then chloride ions would interfere with the determination.

Accessories

- 662 Photometer including 6.1108.010 light guide or 6.5501.00X Spectrode 525 nm

Reagents

- Titrant: barium perchlorate solution, $c[\text{Ba}(\text{ClO}_4)_2] = 0.005 \text{ mol/L}$ in $\phi(\text{isopropanol}) = 85\%$ (volume fraction)
- Indicator solution: 100 mg thorin in 100 mL dist. water
- Perchloric acid, $c(\text{HClO}_4) = 1 \text{ mol/L}$
- Isopropanol, p.a.

Analysis

To 10.0 mL sample solution add 0.3 mL thorin indicator, 1 mL $c(\text{HClO}_4) = 1 \text{ mol/L}$ and 70 mL isopropanol. Degas under vacuum for 30 s, then titrate with $c[\text{Ba}(\text{ClO}_4)_2] = 0.005 \text{ mol/L}$ using the MET mode (volume increment: 0.1 mL, fixed waiting time: 20 s). When working with the 662 Photometer, the transmission is adjusted to 80% at a wavelength of 520 nm prior to the titration.

Calculation

1 mL $c[\text{Ba}(\text{ClO}_4)_2] = 0.005 \text{ mol/L}$ corresponds to 0.4803 mg SO_4^{2-} or 0.1603 mg S

$$\text{mg/L SO}_4^{2-} = \text{EP1} * \text{C01} * \text{C02} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = 10.0 (sample volume in mL)

C01 = 0.4803

C02 = 1000 (conversion factor in mL/L)

Remark

The titer of the barium perchlorate solution diminishes with time and therefore has to be checked regularly [e.g. with $c(\text{H}_2\text{SO}_4) = 0.005 \text{ mol/L}$].

Literature

- Metrohm Application Notes T-7, T-8, T-9 and T-53
Metrohm Ltd., Herisau.
- IP 242/83 (1983)
Sulfur in petroleum products – flask combustion method.
- ISO 680: 1990
Cement – Test methods – Chemical analysis.
- ISO 6844: 1983
Surface active agents – Determination of mineral sulfate content – Titrimetric method.
- ISO 9198: 1989
Paper, board and pulps – Determination of water-soluble sulfates – Titrimetric methods.
- P. Borda
Determination of sulfur in organometallic compounds by the oxygen flask method
Anal. Chim. Acta 196 (1987) 355–357.
- D. Dobcnik, D. Brodnjak-Voncina
Hydrolytic potentiometric titration of sulfate with application to the analysis of water
Anal. Chim. Acta 177 (1985) 209–212.
- 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.
- H. Hwang, P. K. Dasgupta
Microtitration of sulfate with Beryllon II as indicator: determination of sulfate in environmental samples
Mikrochim. Acta 1984/II 159–168.
- M. W. Läubli, O. Dinten, E. Pretsch, W. Simon, F. Vögtle
Barium-selective electrodes based on neutral carriers and their use in the titration of sulfate in combustion products
Anal. Chem. 57 (1985) 2756–2758.
- A. B. Sakla, S. A. Abou Taleb
Simultaneous microdetermination of carbon, hydrogen, chlorine, bromine, sulfur and metals in organometallic compounds
Microchem. J. 28 (1983) 331–340.
- E. P. Scheide, R. A. Durst
Indirect determination of sulfate in natural water by ion-selective electrode
Anal. Lett. 10/1 (1977) 55–65.
- G. T. Weaver, P. K. Khanna, F. Beese
Retention and transport of sulfate in a slightly acid forest soil
Soil Sci. Soc. Am. J. 49 (1985) 746–750.

Figures

```
'fr
751 GPD Titrimetric      01106  751.0020
user                      th
date 1999-10-04         time 15:08      9
card label:Appl.751
U(init)                25 mV MET U      Sulfat W
smp1 size              50 ml
EP1                    2.150 ml          -8 mV
EP2                    7.317 ml          -92 mV
SO4 2-                 4.131 mg/L
stop V reached
=====
```

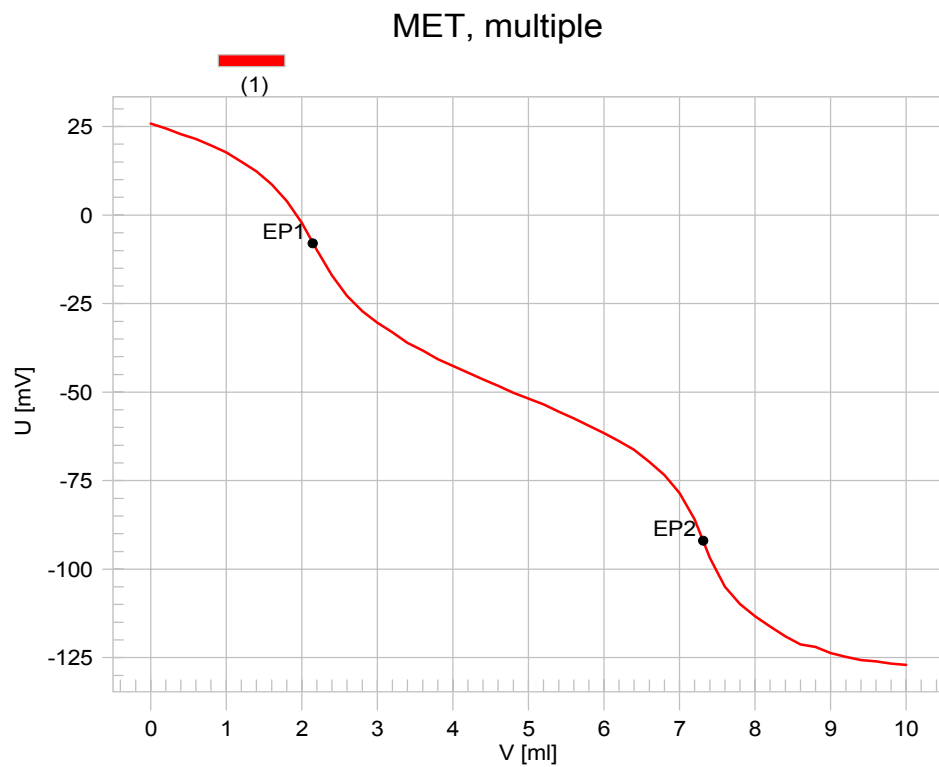


Fig.1: Method 1: determination of sulfate in tap water.

```
'fr
751 GPD Titrimetric 01106 751.0020
user th
date 1999-10-05 time 08:58 1
card label:Appl.751
U(init) -464 mV MET U Sulfat Z
smp1 size 0.04173 g
EP1 5.119 ml -492 mV
SO4 2- 10.474 g/kg
stop V reached
=====
```

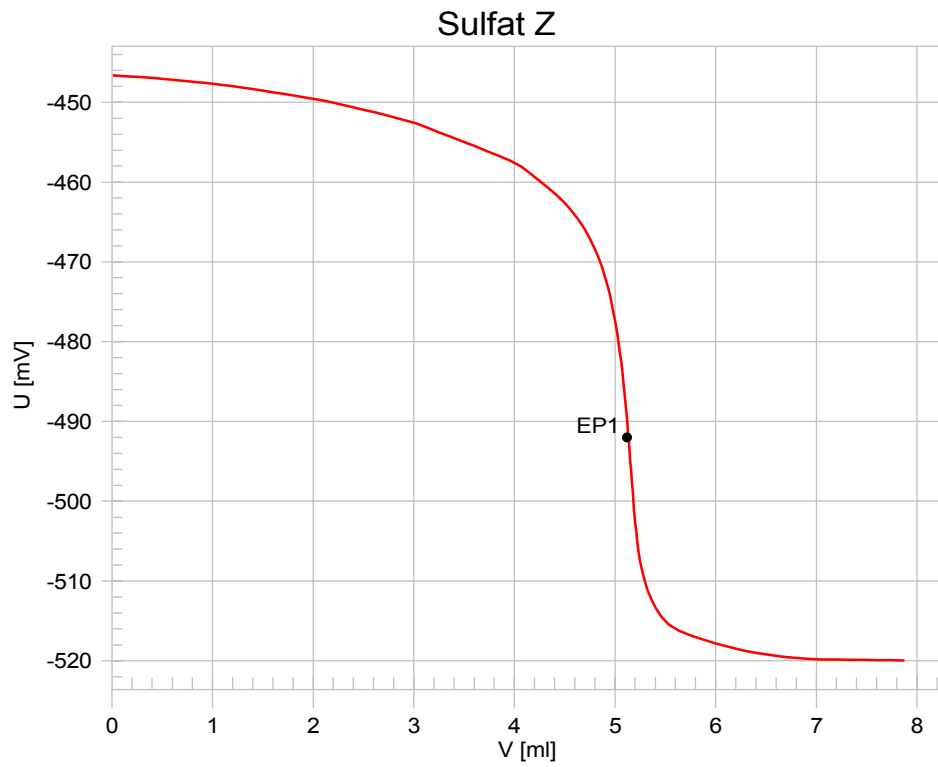


Fig. 2: Method 2: determination of sulfate in cement.

```
'fr
751 GPD Titrimetric 01106 751.0020
user th
date 1999-10-05 time 13:58 9
card label:Appl.751
U(init) -401 mV MET U Sulfat S
smp size 3 ml
EP1 6.390 ml -350 mV
SO4 2- 10.650 mmol/l
SO4 2- 1023.0 mg/L
stop V reached
=====
```

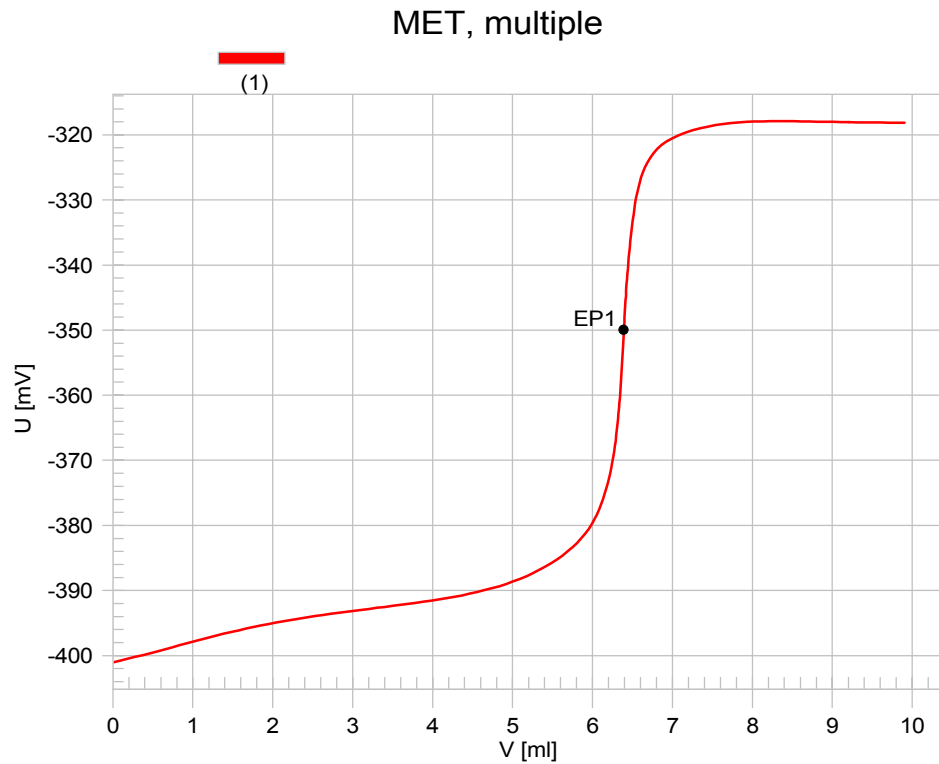


Fig. 3: Method 3: determination of sulfate in a standard solution.

```
'fr
751 GPD Titrimetric      01106  751.0020
user                      th
date 1999-10-07         time 15:19      4
card label:Appl.751
U(init)                220 mV MET U      Sulfat S
smp size                3.0 ml
EP1                    6.193 ml          197 mV
SO4 2-                 10.322 mmol/l
SO4 2-                 991.5 mg/L
stop V reached
=====
```

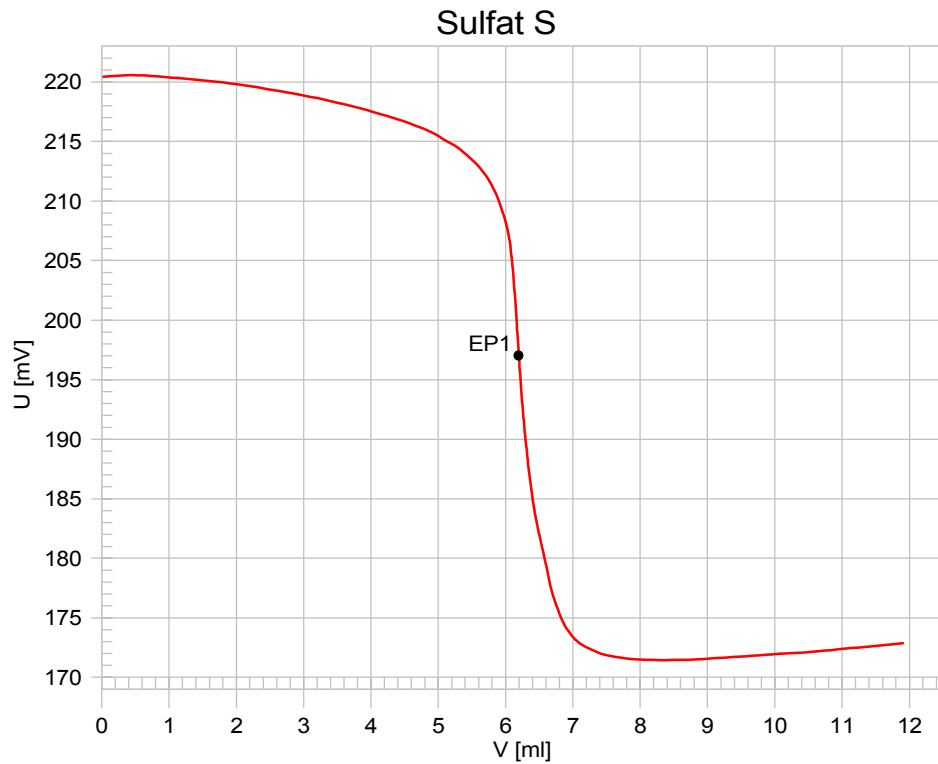


Fig. 4: Method 4: determination of sulfate in an organic substance after digestion.