

# Determination of Sulfate in drinking, surface and waste water

## Description

The determination of the Sulfate is possible using the Ca-ISE and EGTA as titrant. An excess of BaCl<sub>2</sub> is added to the water sample to precipitate the sulfate. The not reacted Ba-ions are back titrated with EGTA titrant. The titration curve shows two equivalence points. The first one corresponds to the Ca and the difference between the second and first EQ corresponds to the Ba. Mg is not determined with this titrant.

## Instruments

|                     |                            |
|---------------------|----------------------------|
| Titration           | TL 7000 or higher          |
| Exchangeable head   | WA 20                      |
| Electrode           | Ca 1100 PLH                |
| Cable               | L 1 A                      |
| Reference electrode | B 2920+                    |
| cable               | L 1 N                      |
| Stirrer             | TM 235                     |
| Lab accessory       | Glass beaker 100 ml        |
|                     | Magnetic stirrer bar 30 mm |

## Reagents

|   |  |
|---|--|
| 1   | EGTA 0.05 mol/l                            |
| 2   | BaCl <sub>2</sub> 0.05 mol/l               |
| 3   | Buffer solution pH 10                      |
| 4   | Distilled Water                            |
| 5   | HCl 2 mol/l, HCL 0.01 mol/l, NaOH 10 mol/l |
| 6   | Ca standard solution 0.1 mol/l             |
| 7   | Electrolyte solution KCL 3 mol/l (L 300)   |
| All reagents should be of analytical grade or better. |  |

## Reagents

### Titration EGTA 0.05 mol/l

19.4 g ethylene glycol-bis-(2-aminoethyl)-tetra acetic acid (98%) is weighed into a beaker and about 200 ml dist. H<sub>2</sub>O are added to mix the EGTA under stirring. Then NaOH 10 mol/l is added until the EGTA is dissolved completely. After cooling down, the solution is transferred quantitatively to a 1000 mL volumetric flask with dist. H<sub>2</sub>O, filled up to the mark and mixed.

The titer determination of the EGTA solution is carried out as described in the application note "Titer determination of EGTA".

### BaCl<sub>2</sub> = 0.05 mol/l

12.34 g BaCl<sub>2</sub> x 2 H<sub>2</sub>O (99%) is weighed out into a 1000 mL volumetric flask, dissolved in HCl = 0.01 mol/l, filled up to the mark with it and mixed.

### Buffer solution pH 10

9 g NH<sub>4</sub>Cl is weighed into a 1000 mL volumetric flask and dissolved in about 800 mL dist. H<sub>2</sub>O. After the addition of 60 mL NH<sub>4</sub>OH = 25% the solution is filled up to the mark with dist. H<sub>2</sub>O and mixed.

### HCl = approx. 2 mol/l

Concentrated HCl is diluted 1:5 with dist. H<sub>2</sub>O.

### Cleaning of the electrode

The electrodes are cleaned with distilled water. The Ca 1100PLH is stored clean and dry, for the storage of the reference electrode use KCl 3 mol/l electrolyte solution (L 300).

## Titration procedure

### Blank titration

A blank titration has to be carried out before. To 40 mL dist. H<sub>2</sub>O are pipetted 5.00 ml of the BaCl<sub>2</sub> 0.05 mol/l solution into the glass beaker. After the addition of 0.5 mL of the Ca standard solution and 5 ml buffer pH 10 the solution is stirred for 3 min. The solution is then back titrated with the EGTA titrant to two EQ's. The difference between the EQ2-EQ1 is stored in the global memory M01.

### Sample preparation

The water sample is pipetted into the glass beaker. The sample volume depends on the expected SO<sub>4</sub> concentration.

The pH is adjusted to pH 4 by adding carefully the HCl 2 mol/l. Then 5 ml of the BaCl<sub>2</sub> 0.05 mol/l solution is added to the sample. After three minutes of reaction time under stirring 5 ml of the buffer solution pH 10 are added. After additional three minutes of reaction time the sample is back titrated with the EGTA titrant to two EQ's.

## Titration parameter

### Blank value

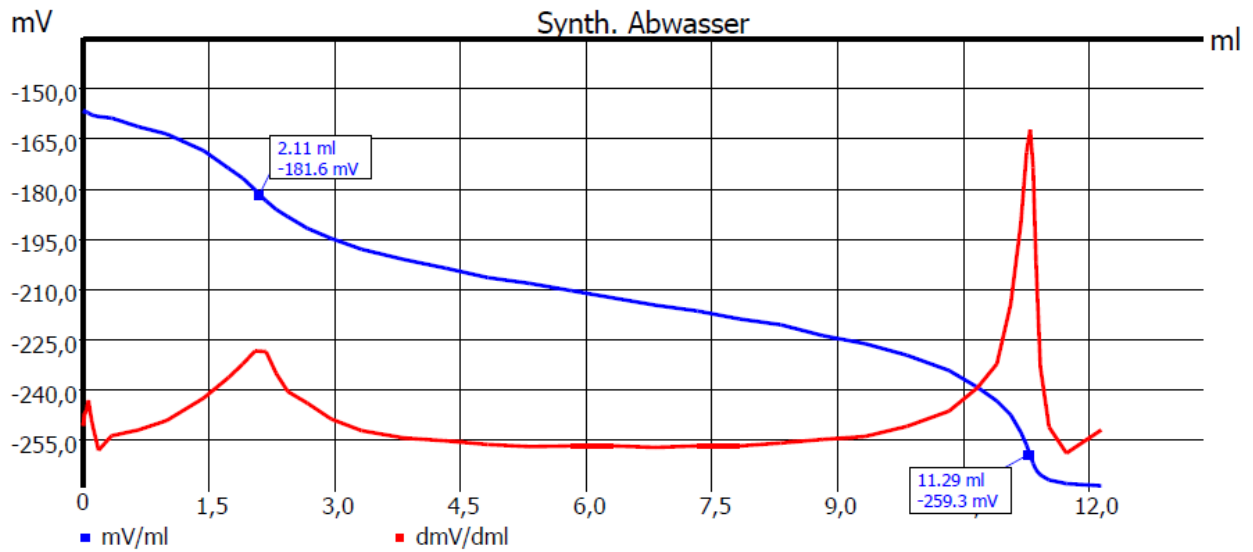
|                         |                     |                      |          |
|-------------------------|---------------------|----------------------|----------|
| Default method          | ---                 |                      |          |
| Method type             | Automatic titration |                      |          |
| Modus                   | Dynamic             |                      |          |
| Measured value          | mV                  |                      |          |
| Measuring speed / drift | User defined        | Minimum holding time | 5 s      |
|                         |                     | Maximum holding time | 12 s     |
|                         |                     | Measuring time       | 4 s      |
|                         |                     | Drift                | 3 mV/min |
| Initial waiting time    | 10 s                |                      |          |
| Dynamic                 | flat                | Max step size        | 0.5 ml   |
|                         |                     | Slope max ml         | 10       |
|                         |                     | Min. step size       | 0.05 ml  |
|                         |                     | Slope min. ml        | 50       |
| Damping                 | none                | Titration direction  | decrease |
| Pretitration            | off                 | Delay time           | 0 s      |
| End value               | off                 |                      |          |
| EQ                      | On (2)              | Slope value          | 120      |
| Max. titration volume   | 20 ml               |                      |          |
| Dosing speed            | 100%                | Filling speed        | 30 s     |

Calculation:

$$\text{Result EQ1} = EQ1$$

$$\text{Result blank value [ml]} = EQ2 - EQ1$$

## Sample titration



|                         |                     |                      |          |
|-------------------------|---------------------|----------------------|----------|
| Default method          | ---                 |                      |          |
| Method type             | Automatic titration |                      |          |
| Modus                   | Dynamic             |                      |          |
| Measured value          | mV                  |                      |          |
| Measuring speed / drift | User defined        | Minimum holding time | 5 s      |
|                         |                     | Maximum holding time | 12 s     |
|                         |                     | Measuring time       | 4 s      |
|                         |                     | Drift                | 3 mV/min |
| Initial waiting time    | 10 s                |                      |          |
| Dynamic                 | flat                | Max step size        | 0.5 ml   |
|                         |                     | Slope max ml         | 10       |
|                         |                     | Min. step size       | 0.05 ml  |
|                         |                     | Slope min. ml        | 50       |
| Damping                 | none                | Titration direction  | decrease |
| Pretitration            | off                 | Delay time           | 0 s      |
| End value               | off                 |                      |          |
| EQ                      | On (2)              | Slope value          | 120      |
| Max. titration volume   | 20 ml               |                      |          |
| Dosing speed            | 100%                | Filling speed        | 30 s     |

Calculation:

$$\text{Result } Ca^{2+} [mg/l] = \frac{EQ1 * T * M_{Ca} * 1000}{V}$$

$$\text{Result } SO_4^{2-} [mg/l] = \frac{((M01 - (EQ2 - EQ1)) * T * M_{SO_4} * 1000}{V}$$

|                             |       |  |
|-----------------------------|-------|--|
| EQ1                         |       | Consumption of titrant at first Equivalence point      |
| EQ2                         |       | Consumption of titrant at second Equivalence point     |
| T                           | WA    | Actual concentration of the titrant (e.g.0.0511 mol/l) |
| M <sub>Ca</sub>             | 40,08 | Molecular mass of Ca                                   |
| M <sub>SO<sub>4</sub></sub> | 96,06 | Molecular mass of SO <sub>4</sub>                      |
| V                           | man   | sample volume [ml]                                     |