SLOVENSKI STANDARD
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Kakovost vode - Določanje sulfata - Gravimetrijska metoda z uporabo barijevega klorida

Water quality -- Determination of sulfate -- Gravimetric method using barium chloride

Qualité de l'eau -- Dosage des sulfates -- Méthode gravimétrique au chlorure de baryum

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INTERNATIONAL STANDARD

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Water quality — Determination of sulfate — Gravimetric method using barium chloride

Qualité de l'eau — Dosage des sulfates — Méthode gravimétrique au chlorure de baryum

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9280 was prepared by Technical Committee ISO/TC 147, *Water quality*.

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Water quality — Determination of sulfate — Gravimetric method using barium chloride

1 Scope

This International Standard specifies a gravimetric method for the determination of sulfate in water. The method is applicable to the analysis of all types of water, including sea water and most industrial effluents. For information on potentially interfering substances, see clause 8.

A sulfate concentration (expressed as SO_4^{2-}) in the range of 10 mg/l to 5 000 mg/l can be determined using the specified test portion (6.1). It is possible to determine higher concentrations after dilution of the laboratory sample.

The lower limit of detection (with nine degrees of freedom) is

$$SO_4^{2-} = 10 \text{ mg/l}$$

2 Principle

Acidification of the sample with hydrochloric acid followed by boiling with barium chloride solution for at least 20 min to promote coagulation of the precipitate of barium sulfate. Filtration through a tared sintered-glass crucible, washing the precipitate free from chloride, drying at 105 °C and reweighing when cool. The increase in mass of the crucible is due to the barium sulfate precipitate formed by reaction of barium with sulfate ions in the sample.

3 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.1 Hydrochloric acid, $c(\text{HCl}) = 6$ mol/l.

With care, mix 500 ml ± 10 ml of concentrated hydrochloric acid [$\rho(\text{HCl}) = 1{,}18$ g/ml] with water and dilute to 1 litre in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

3.2 Barium chloride, dihydrate solution, 100 g/l.

WARNING — Barium chloride is poisonous and harmful if swallowed.

Dissolve 100 g ± 1 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in about 800 ml of water, warming the mixture to aid dissolution. Cool the solution and dilute to 1 litre with water in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

3.3 Sodium hydroxide solution, $c(\text{NaOH}) = 5$ mol/l.

WARNING — Sodium hydroxide solution is hazardous on contact with skin and eyes.

Dissolve 20,0 g of sodium hydroxide in 100,0 ml of water, whilst stirring.

Store in a polyethylene bottle.

3.4 Methyl orange, indicator solution, about 1 g/l.

Dissolve 100 mg of methyl orange in about 50 ml of water, warming the mixture to aid dissolution. Cool the solution and dilute to 100 ml with water in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

3.5 Silver nitrate solution, about 0,1 mol/l.

Dissolve 17 g ± 1 g of silver nitrate, $AgNO_3$, in about 800 ml of water and dilute to 1 litre in a measuring cylinder.

Store in an amber glass bottle. The solution is stable indefinitely if protected from light.

3.6 Ethanol, C_2H_5OH, or rectified spirit (95 % ethanol, 5 % methanol).

3.7 Sodium chloride solution, 100 g/l.

Dissolve 10,0 g ± 0,1 g of sodium chloride, NaCl, in about 100 ml of water.

Store in a glass or polyethylene bottle.

3.8 Sodium carbonate, Na_2CO_3, anhydrous.

4 Apparatus

4.1 Sintered-glass crucibles, of capacity about 30 ml, porosity value of 4.

4.2 Buchner flask, equipped with safety guard for vacuum filtration.

4.3 Analytical balance, capable of weighing to at least 0,000 2 g.

4.4 Platinum evaporating dish, of capacity 250 ml.

5 Sampling and sample preparation

5.1 Sampling

Collect samples in glass or polyethylene bottles and analyze on the day of collection or store at 2 °C to 5 °C for not more than one week.

Fill the sample bottles completely to exclude air and thus eliminate the risk of oxidation of samples containing sulfide or sulfite.

NOTE 1 Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that samples are sufficiently stable.

5.2 Preparation of test sample

For the determination of sulfate in solution allow any suspended solids to settle prior to withdrawing the test portion (6.1). Alternatively, filter the laboratory sample through a fine porosity, ashless filter paper in order to prepare a test sample.

6 Procedure

6.1 Test portion

The test portion volume shall be between 10 ml and 200 ml and shall contain not more than 50 mg of sulfate ions. Using a pipette, withdraw the test portion from the settled test sample (see 5.2).

NOTE 2 For shaken test samples containing large amounts of suspended solids it may be necessary to measure the test portion in a measuring cylinder, but with a likely consequent decrease in the accuracy and precision of the method.

6.2 Pretreatment

6.2.1 Measure the test portion (6.1) into a 500 ml beaker and add 2 drops of methyl orange indicator (3.4). Neutralize the test portion with hydrochloric acid (3.1) or sodium hydroxide solution (3.3) depending on the initial pH. Add 2 ml ± 0,2 ml of hydrochloric acid and then, if necessary, add water to bring the total volume in the beaker to 200 ml ± 20 ml. Boil the contents of the beaker for at least 5 min.

If the solution is clear after boiling, proceed to 6.3. If insoluble material is present, filter the hot mixture through a fine porosity, ashless filter paper and wash the filter piper with a small amount of hot water, combining the washing with the filtrate. Transfer the solution quantitatively to a 500 ml beaker and proceed to 6.3.

6.2.2 If it is suspected that the insoluble material retained by the filter paper contains insoluble sulfate and it is desired to include this in the final result, retain the filter paper and carry out the procedure given in 9.2.

6.2.3 If silica is present in the test portion at concentrations likely to interfere (see clause 8), follow the pretreatment method given in 9.1.

6.2.4 If organic substances are present in the test portion at concentrations likely to interfere (see clause 8), follow the pretreatment method given in 9.1.

6.3 Precipitation

Boil the solution produced at the end of the pretreatment (6.2) and slowly add, using a pipette, 10 ml ± 1 ml of hot (about 80 °C) barium chloride solution (3.2). Heat the solution for at least 1 h, cover and allow to cool and stand overnight at 50 °C ± 10 °C.

NOTE 3 Slow addition of the hot barium chloride reduces the possibility of coprecipitation. Subsequent heating aids coagulation of the precipitate and renders it more crystalline, reducing coprecipitation even further.

6.4 Filtration

6.4.1 Procedure

Dry a sintered-glass crucible (4.1) by heating it to 105 °C for 1 h and let it cool in a desiccator.

Accurately weigh the crucible (to the nearest 0,000 2 g) and then fit it on a Buchner flask (4.2). Filter the precipitate using gentle suction. Use a rubber-tipped glass rod to dislodge any precipitate remaining in the beaker and rinse with cold water into the crucible. Wash the precipitate in the crucible with chloride-free cold water.

6.4.2 Test for chloride in the washings

Collect about 5 ml of the filtrate from 6.4.1 in a small beaker containing about 5 ml of silver nitrate solution (3.5). To ascertain whether the washings and hence the barium sulfate precipitate are free from chloride, observe the mixture and check that no turbidity is formed. Otherwise continue washing.

NOTE 4 It is also important to check that no chloride remains on the rim of the underside of the crucible.

6.5 Drying and weighing

Remove the crucible and dry it at 105 °C ± 2 °C for about 1 h. Transfer the crucible to a desiccator and weigh it when it has cooled to room temperature so that the mass is accurately known. Return the crucible to the drying oven for a further 10 min and repeat the cooling and weighing. Provided that the second mass differs by not more than 0,000 2 g from the first, record the second mass. Otherwise repeat the drying, cooling and weighing until two successive masses do not differ by more than 0,000 2 g.

NOTE 5 Shorter drying periods may be obtained if the precipitate is washed with three 5 ml portions of ethanol (3.6).

6.6 Blank test

For a check of crucibles to be used in the test follow a procedure identical to that given in 6.3 to 6.5, but using 200 ml ± 20 ml of water.

Subtract the crucible mass recorded before filtration as in 6.4 from that recorded after filtration as in 6.5 to obtain the blank mass in grams.

NOTE 6 If filtration is necessary during sample pretreatment (6.2), the portion of water used in the blank test shall first be filtered as described in the second paragraph of 6.2.1, unless previous tests have demonstrated that no contribution to the blank arises from filtration.

7 Expression of results

7.1 Calculation

Calculate the mass of barium sulfate in the test sample, m, in grams, from the following equation:

$$m = m_2 - m_1 - m_0 \qquad \ldots (1)$$

where

m_0 is the blank mass, in grams, calculated in 6.6;

m_1 is the crucible mass, in grams, recorded in 6.4;

m_2 is the crucible mass, in grams, recorded in 6.5.

Calculate the sulfate concentration, in milligrams per litre as SO_4^{2-} from the following equation:

$$\frac{m \times 1000 \times 0{,}4116}{V} \qquad \ldots (2)$$

where

m is the mass of barium sulfate precipitate, in grams;

V is the test portion volume, in millilitres (see 6.1);

0,411 6 is the gravimetric factor.

Table 1 — Conversion factors for other units of concentration (c)

	SO_4^{2-} mg/l	$c(SO_4^{2-})$ mmol/l	Sulfur S mg/l
SO_4^{2-} = 1 mg/l	1	0,010 41	0,333 8
$c(SO_4^{2-})$ = 1 mmol/l	96,06	1	32,06

7.2 Precision

Repeatability and reproducibility standard deviations have been determined as shown in table 2.

Table 2 — Repeatability and reproducibility standard deviations

Sample	Test portion volume ml	Sulfate concentration mg/l	σ_r mg/l	CV$_r$ %	σ_R mg/l	CV$_R$ %
1	200	50	3,3			
2	20	210	3,3	1,6	6,9	3,3
3	20	583	8,4	1,4	12,9	2,1
4	20	1 160	9,3	0,8	11,6	1,0
5	20	1 500	21,3			
6	20	5 000	28,4			

where

σ_r is the repeatability standard deviation;

CV$_r$ is the repeatability variation coefficient;

σ_R is the reproducibility standard deviation;

CV$_R$ is the reproducibility variation coefficient.

1, 5, 6: Standard solutions, data from United Kingdom, one laboratory, nine degrees of freedom.

2: Data from Germany, F.R., 10 laboratories, 37 degrees of freedom.

3: Data from Germany, F.R., 10 laboratories, 35 degrees of freedom.

4: Data from Germany, F.R., 9 laboratories, 32 degrees of freedom.

Table 3 — Tolerance to other ions

Ions	Expressed as	Maximum mass in the test portion mg
Chromate	CrO_4^{2-}	10
Phosphate	PO_4^{2-}	10
Nitrate	NO_3^{2-}	100
Silicate	SiO_2^{2-}	2,5
Calcium	Ca^{2+}	100
Iron(III)	Fe^{3+}	50

8 Interferences

Sulfide and sulfite could interfere if samples are unduly exposed to air causing oxidation to sulfate to occur before analysis. Otherwise, any sulfides and sulfites present at the beginning of the analysis are removed as hydrogen sulfide and sulfur dioxide gases respectively, by boiling during pretreatment (6.2).

Organic compounds present in substantial amounts (for example a sample with a permanganate index > 30 mg/l O_2) may interfere by absorption or coprecipitation. Follow the procedure given in clause 9 to overcome this difficulty.

Amounts in the test portion (6.1) of other inorganic ions, below which no interference is likely, are given in table 3.

9 Special cases

9.1 Removal of organic compounds

Measure the test portion (6.1) into a platinum evaporating dish (4.4) and add two drops of methyl orange indicator (3.4).

Neutralize the test portion with hydrochloric acid (3.1) or sodium hydroxide (3.3) according to the initial pH and then add 2,0 ml of hydrochloric acid. Evaporate almost to dryness on a water bath and then add five drops of sodium chloride solution (3.7) to the remaining liquid. Evaporate to complete dryness and then heat the dish to a dull red heat (about 700 °C) over a bunsen flame or in a muffle furnace to form an ash.

Allow to cool and then moisten the ash with about 10 ml of water. Add five drops of hydrochloric acid (3.1) and evaporate to dryness on a water bath. Then allow to cool slightly, add 3 ml ± 1 ml of water and warm the mixture in the basin to near boiling point. Then proceed as described in 6.2, beginning with "... filter the hot mixture..." in the second paragraph of 6.2.1.

9.2 Determination of sulfate in insoluble material

9.2.1 Place the filter paper from 6.2.2 in a platinum dish (4.4) covered with a lid and either heat over a low bunsen flame or place it in a muffle furnace at room temperature and bring the muffle furnace up to a temperature of 500 °C to burn off the paper. Mix the ignited residue with 4 g ± 0,1 g of anhydrous sodium carbonate (3.8) and heat strongly to fuse the mixture, maintaining it in a melted state for 15 min. Allow to cool.