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Water quality — Determination of sulfates — Method by continuous flow analysis (CFA)

Qualité de l'eau — Dosage des sulfates — Méthode par analyse en flux continu (CFA)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 22743 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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Introduction

Methods using flow analysis automate wet chemical procedures and are particularly suitable for the processing of many analytes in water in large sample series at a high analysis frequency.

Analysis can be performed by flow injection analysis (FIA) [1], [2] or by continuous flow analysis (CFA) [3]. Both methods share the feature of an automatic dosage of the sample into a flow system (manifold) where the analytes in the sample react with the reagent solutions on its way through the manifold. The sample preparation may be integrated in the manifold. The reaction product is measured in a flow detector (e.g. flow photometer). The detector produces a signal from which the concentration of the parameter is calculated.

It is necessary to examine whether and to what extent particular problems will require the specification of additional marginal conditions.

In this International Standard, only the CFA procedure is described.

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Water quality — Determination of sulfates — Method by continuous flow analysis (CFA)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a continuous flow analysis (CFA) method for the determination of sulfate in various types of water (such as ground water, drinking water and waste water).

The method is applicable to samples with a sulfate (SO_4) mass concentration from 30 mg/l to 300 mg/l. Other concentration ranges are applicable, provided they cover exactly one decade of concentration units (e.g. 100 mg/l to 1 000 mg/l).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

3 Interferences

Calcium-, magnesium-, iron- and aluminium ions interfere with the determination of sulfate (negative bias). Treatment with a cation exchange resin will reduce the interferences.

Sulfide, sulfite, phosphate and tannic acids may lead to a positive bias, but concentrations of these substances which cause measurable interferences are usually not found in real samples.

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4 Principle

Sulfate reacts in an acidic solution with barium chloride to form barium sulfate. The excessive barium chloride reacts with methylthymol blue in an alkaline solution to a chelated barium methylthymol blue. The absorbance of the free non-chelated methylthymol blue is measured at 460 nm ± 10 nm in a flow through detector. Other metals, such as calcium, magnesium, iron and aluminium, are removed by an ion exchange column prior to the reactions with barium.

5 Reagents

Use analytical grade chemicals, unless otherwise specified, and check the blank value of the reagents.

5.1 Water, complying with grade 1 as defined in ISO 3696.

5.2 Barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$.

5.3 Concentrated hydrochloric acid, $c(HCl) = 12$ mol/l, $\rho(HCl) = 1{,}19$ g/ml.

5.4 Methylthymol blue, ($C_{37}H_{40}N_2O_{13}SNa_4$ or $C_{37}H_{43}N_2O_{13}SNa$).

5.5 Surfactant, polyoxyethylene-23-laurylether ($C_{12}H_{25}(OCH_2CH_2)_{23}OH$), a mass fraction of 30 % solution in water.

5.6 Sodium hydroxide, (NaOH).

5.7 Ethylenedinitrilotetracetic acid tetrasodium salt, Na_4-EDTA, ($C_{10}H_{12}N_2Na_4O_8$).

5.8 Ammonium chloride, (NH_4Cl).

5.9 Ammonia solution, 25 % solution, $c(NH_3 \cdot H_2O) = 14$ mol/l, $\rho(NH_3 \cdot H_2O) = 0{,}91$ g/ml.

5.10 Ethanol, C_2H_5OH, a volume fraction of 96 %, $\rho = 0{,}79$ g/ml, food grade or pure grade.

5.11 Sodium sulfate, (Na_2SO_4), dried for 2 h at 105 °C.

5.12 Cation exchange resin, DOWEX 50W-X8 1), particle size 0,3 mm to 0,8 mm in H^+ form.

5.13 Barium chloride solution

In a 1 000 ml volumetric flask, dissolve 917 mg ± 1 mg of barium chloride dihydrate (5.2) in about 500 ml of water (5.1) and make up to volume with water (5.1).

When stored at 2 °C to 6 °C, the solution is stable for 1 month.

5.14 Diluted hydrochloric acid, $c(HCl) = 1$ mol/l.

In a 1 000 ml volumetric flask, dilute 82 ml of concentrated hydrochloric acid (5.3) in about 800 ml of water (5.1) and make up to volume with water (5.1).

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1) DOWEX 50W-X8 is a trade name. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

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5.15 Methylthymol blue solution

In a 1 000 ml volumetric flask, dissolve 160 mg ± 1 mg of methylthymol blue (5.4) in 50 ml of barium chloride solution (5.13). Add 4 ml of concentrated hydrochloric acid (5.3) and 360 ml of ethanol (5.10). Make up to volume with water (5.1). Add 1 ml of surfactant (5.5).

When stored at 2 °C to 6 °C, the solution is stable for 1 week.

5.16 Buffered Na_4-EDTA solution, pH = 10,5.

In a 1 000 ml volumetric flask, dissolve 6,75 g of ammonium chloride (5.8) and 40,0 g of Na_4-EDTA (5.7) in about 500 ml of water (5.1). Add 57 ml of ammonia solution (5.9) and make up to volume with water (5.1).

5.17 Sodium hydroxide solution, $c(NaOH) = 0{,}25$ mol/l.

In a 1 000 ml volumetric flask, dissolve 10,0 g of sodium hydroxide (5.6) in about 500 ml of water (5.1). Make up to volume with water (5.1).

5.18 Sulfate stock solution, $\rho(SO_4) = 3\,000$ mg/l.

In a 1 000 ml volumetric flask, dissolve (4 436 ± 1) mg of sodium sulfate (5.11) in about 500 ml of water (5.1). Make up to volume with water (5.1).

5.19 Sulfate spiking solution, $\rho(SO_4) = 6$ mg/l.

In a 1 000 ml volumetric flask, dilute 2,00 ml of sulfate stock solution (5.18) in about 800 ml of water (5.1). Make up to volume with water (5.1). Add 1 ml of surfactant (5.5).

NOTE The sulfate solution is added to achieve better linearity in the lower measuring part of the calibration curve. In respect to the sulfate concentration in the blank or the quality of the methylthymol blue (5.4), the added sulfate amount can be slightly altered. Without the sulfate addition, this lower part will not be linear.

5.20 Calibration solutions

Prepare at least five calibration solutions by diluting the sulfate stock solution (5.18).

Table 1 gives examples for the preparation of 10 calibration solutions in the range of 30 mg/l to 300 mg/l.

Table 1 — Example for preparation of 10 calibration solutions for the sulfate (SO_4) range 30 mg/l to 300 mg/l

Volume in ml of sulfate stock solution (5.18) diluted to 100 ml	1	2	3	4	5	6	7	8	9	10
Sulfate (SO_4) concentration of calibration solution in mg/l	30	60	90	120	150	180	210	240	270	300

6 Apparatus

6.1 Continuous-flow analysis (CFA).

The system generally consists of the following components (see Figure A.1 in Annex A).

6.1.1 Sampler or other device, for reproducible sample introduction.

6.1.2 Reagent containers.

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6.1.3 Low pulse pump, with chemical resistant pump tubes.

6.1.4 Inlet connector, made of glass, or chemical resistant material, with reproducible air-, sample- and reagent segmentation.

6.1.5 Photometer, with flow cell, optical path length, e.g. 10 mm, wavelength range 450 nm to 470 nm.

6.1.6 Data acquisition and display unit, such as a PC, recorder, printer or plotter.

6.2 Graduated flasks, nominal capacity 100 ml and 1 000 ml.

6.3 Graduated pipettes, nominal capacity 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml, 10 ml and 50 ml.

6.4 Cation exchange column.

Glass tube with a length of at least 10 cm and an internal diameter of approximately 2 mm. Suspend the cation exchange resin in water (5.1) and fill the tube with this mixture. Close both sides of the tube with approximately 5 mm of glass wool.

7 Sampling and sample pretreatment

Carry out sampling as specified in ISO 5667-3. Prior to use rinse all containers which will come into contact with the sample with water (5.1).

The samples may be stored in either glass or plastics containers for at least one month. Sample preservation is not required (see ISO 5667-3). Prior to analysis, filter the sample, if necessary.

8 Procedure

8.1 Preparation for the analyses

Set up the flow analyser for the desired procedure (see Figure A.1 in Annex A).

Pump hydrochloric acid (5.14) for 15 min to regenerate the cation exchange column (6.4). Use the pump tube for the sulfate spiking solution (5.19). Rinse the column by pumping water (5.1) through the column for 10 min.

Pump the reagents (see Figure A.1) for up to 15 min and set the baseline to zero.

The analyser is operational when there is no baseline drift.

Proceed in accordance with 8.2 to 8.5.

8.2 Quality requirements for the measuring system

8.2.1 Instrument performance checks

The following requirements apply.

a) In the analytical system, prepared according to 8.1, a calibration solution (5.20) with a sulfate concentration of about 100 mg/l shall exhibit an absorbance per centimetre of at least 0,260 cm^{-1}. Otherwise, the flow system is not suitable, and it shall be replaced by a system which fulfill this requirement.

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If the photometric detector (6.1.5) does not allow any absorbance readings, the absorbance may be determined by comparing an external absorbance measuring photometer. In this case, a sufficient quantity of the reaction mixture (containing the sample) and the appropriate reagent solutions (see Clause 5) should be prepared manually and measured in the external photometer.

b) A calibration solution (5.20) with a sulfate concentration of 30 mg/l shall exhibit a signal to noise relation of at least 3:1.

8.2.2 Daily sensitivity test

If a recorder is used for the measurement, transfer the sample probe into a sulfate calibration solution (5.20; e.g. 300 mg/l, depending on the full-scale range) after stabilization of the baseline. When there is a positive response at the registration unit, due to the colour produced from the calibration solution, adjust the response to read about 95 % of full-scale deflection.

8.3 Calibration

Calibrate each range with at least five calibration solutions (5.20), with concentrations equidistantly distributed over the working range, and water (5.1) as reagent blank.

Select the appropriate calibration solutions (5.20).

If different working ranges are applied, carry out a separate calibration for each working range.

Before starting the analysis, set the baseline as recommended by the instrument manufacturer, or as appropriate.

Analyse by sequentially applying the calibration solutions and reagent blanks and obtain the measured values corresponding to the solutions applied.

Calculate the calibration curve according to ISO 8466-1.

If the linearity test described in ISO 8466-1 shows that the calibration curve is not linear, calculate the calibration curve as specified in ISO 8466-2.

The analysis conditions for standards and samples are identical (see 8.4). The output signal is proportional to the sulfate concentration.

The following Equations (1) and (2) are used:

For linear curves:

$$y = a + b\rho \tag{1}$$

For non-linear curves:

$$y = a + (b\rho) + (c\rho^2) \tag{2}$$

where

y is the measured value, in system related units;

a is the calibration curve intercept, in system related units;

b is a coefficient of the calibration function, in system related units × litres per milligram;

c is a coefficient of the calibration function, in system related units × litres^2 per milligram^2;

ρ is the mass concentration of sulfate, in milligrams per litre, mg/l.

8.4 Measurement

Analyse samples in the same way as the calibration solutions.

If the sample concentration is higher than the selected working range, analyse the sample in a different range or dilute it prior to analysis.

After each group of sample measurements, at the latest after every 20 measurements, check the system calibration using one calibration solution (5.20) each for the lower and upper parts of the respective working range. If the results of these two solutions lie outside the confidence range of the calibration curve (see ISO 8466-1), re-calibrate the system.

8.5 Closing down the system

Rinse the system by connecting the pump tubes of the methylthymol blue reagent (5.15) and sodium hydroxide solution (5.17) with the Na_4-EDTA solution (5.16). After 15 min, replace the Na_4-EDTA solution with water (5.1) and rinse for 15 min.

9 Calculation of results

Calculate the mass concentration of sulfate in the samples using the Equations (3), (4) and (5):

For linear curves:

$$\rho = (y - a)/b \tag{3}$$

For non-linear curves with negative curvature:

$$\rho = -\frac{b}{2c} - \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a-y}{c}} \tag{4}$$

For non-linear curves with positive curvature:

$$\rho = -\frac{b}{2c} + \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a-y}{c}} \tag{5}$$

For an explanation of the symbols, see 8.3.

Calculate the mass concentration of sulfate in samples according to the calibration range they fall into. Do not extrapolate a calibration curve higher than the highest calibration solution.

10 Expression of results

Report results in milligrams per litre (mg/l) or grams per litre (g/l) in not more than 2 significant figures.

EXAMPLES

Mass concentration of sulfate:	35 mg/l
Mass concentration of sulfate:	0,14 g/l

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11 Test report

This clause specifies which information is to be included in the test report. The clause shall require information to be given on at least the following aspects of the test:

a) a reference to this International Standard (ISO 22743:2006);

b) identity of the sample;

c) sample preparation;

d) description of the analyser type or flow conditions used;

e) results, according to Clause 10;

f) any deviation from this standard or any circumstances which may have affected the results.

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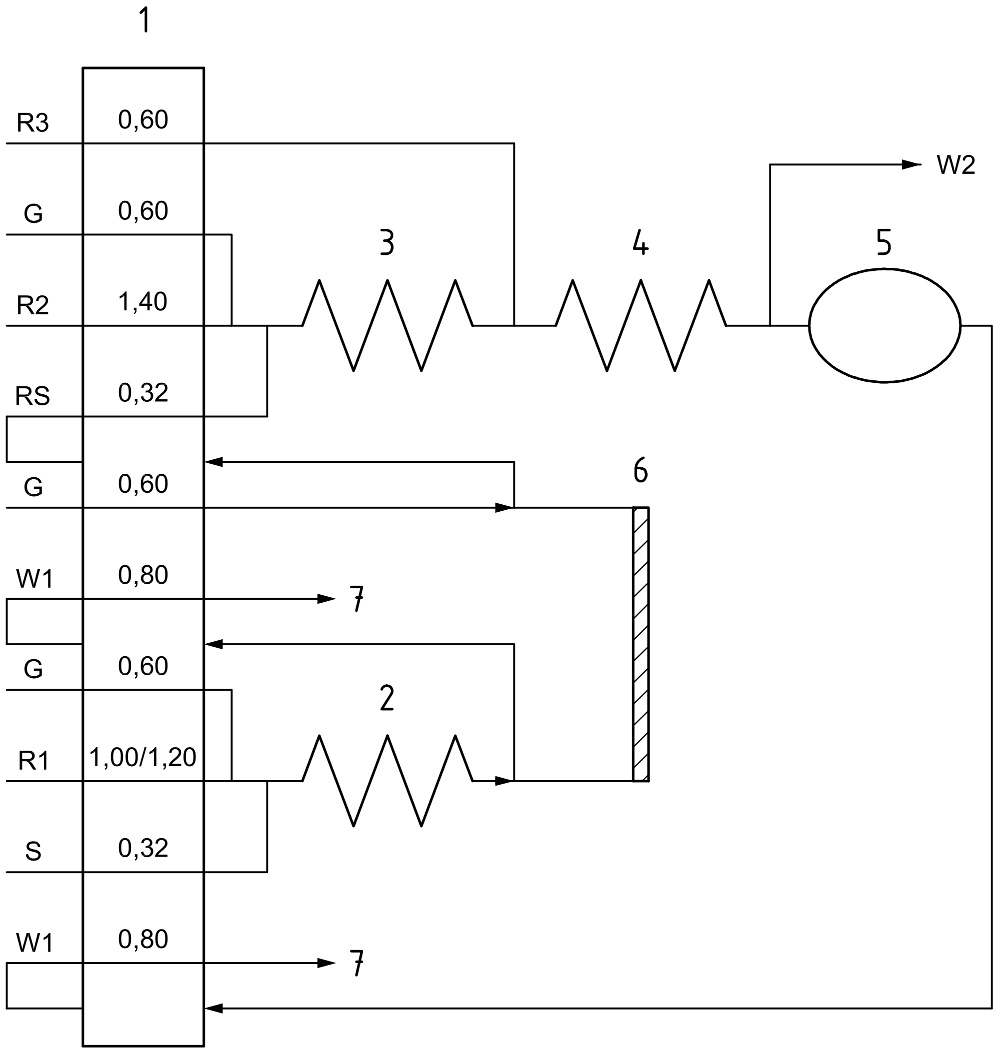
Annex A
(informative)

Example of a CFA system for the determination of sulfate



Key

1	pump, flow rates in ml/min
2	reaction coil, length:70 cm, internal diameter: 1,5 mm
3	reaction coil, length: 135 cm, internal diameter: 1,5 mm
4	reaction coil, length: 135 cm, internal diameter: 1,5 mm
5	detector, optical path length: 10 mm, wavelength: 460 nm ± 10 nm
6	ion-exchange column, length: 30 cm, internal diameter: 2,0 mm
7	waste
G	air, flow rate: 0,60 ml/min
S	original sample, flow rate: 0,32 ml/min
RS	sample after column treatment, flow rate: 0,32 ml/min
R1	sulfate spiking solution (5.19), flow rate: 1,00 ml/min or 1,20 ml/min
R2	methylthymol blue solution (5.15), flow rate: 1,40 ml/min
R3	sodium hydroxide solution (5.17), flow rate: 0,60 ml/min
W1	de-bubbled reaction mixture transported to the waste, flow rate: 0,80 ml/min
W2	air bubbles with a small amount of the reaction mixture

Figure A.1 — Determination of sulfate by CFA in the range 30 mg/l to 300 mg/l

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Annex B
(informative)

Precision and accuracy

The statistical data in Table B.1 were obtained by an interlaboratory trial carried out in February 2005.

Table B.1 — Performance data for the determination of sulfate by CFA (number of participants: 14)

Sample[a]	**Matrix**	l	n	n_{AP} %	x_{exp} mg/l	x mg/l	η %	s_R mg/l	CV$_R$ %	s_r mg/l	CV$_r$ **%**
1	Drinking water	14	55	1,8	292	281,4	96	16,27	5,782	3,588	1,275
2	Surface water	13	52	7,1	188	188	100	6,589	3,505	1,772	0,943
3	Waste water	13	52	7,1	66,8	63,4	95	4,186	6,603	0,794	1,252

l	is the number of laboratories (outlier-free) (target value: $\geqslant 8$);
n	is the number of outlier-free individual analytical values (target value: $\geqslant 24$);
n_{AP}	is the relative portion of outliers (target value: $\leqslant 25$ %);
x_{exp}	is the accepted true value;
x	is the total mean, depending on outlier-free values;
η	is the recovery rate;
s_R	is the reproducibility standard deviation;
CV$_R$	is the reproducibility coefficient of variation (target value: $\leqslant 25$ %);
s_r	is the repeatability standard deviation;
CV$_r$	is the repeatability coefficient of variation.

NOTE 1 According to ISO 5725-2, a replacement of outliers of type “C” was not performed if the internal coefficients of variation were not higher than 2,5 %.

NOTE 2 The accepted true values were determined using the LC method of ISO 10304-1, ISO 10304-2 (laboratories of the Technical University, Berlin, and the State Laboratory of Hessia, Wiesbaden).

[a] Applied samples:

1	Drinking water (City of Berlin)
2	Surface water (Landwehrkanal, Berlin)
3	Domestic waste water (City of Berlin)

Bibliography

[1] RUZICKA, J., HANSEN, E.H. *Flow Injection Analysis*, published by Wiley & Sons, 1981

[2] MÖLLER, J. *Flow Injection Analysis*, Analytiker Taschenbuch, Bd. 7, published by Springer Verlag, 1988, pp. 199 to 275, in German

[3] SKEGGS, L.T. *Anal. Chem.*, **38**(6), 1966, 31 A

[4] APHA/AWWA/WEF, Standard methods for the examination of water and waste water. 1998, 20th edition, 4-179 to 4-181

[5] COLOVOS, G., PANESAR, M.R., PARRY, E.P. Linearizing the calibration curve in determination of sulfate by the methylthymol blue method, *Anal. Chem*. **48**(12), 1976, pp. 1693-1696

[6] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[7] ISO 10304-1, *Water quality — Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions — Part 1: Method for water with low contamination*

[8] ISO 10304-2, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste water*

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