



SLOVENSKI STANDARD

SIST EN 1485:1997

01-avgust-1997

Kakovost vode - Določanje adsorblijivih organsko vezanih halogenskih spojin (AOX)

Water quality - Determination of adsorbable organically bound halogens (AOX)

Wasserbeschaffenheit - Bestimmung adsorbierbarer organisch gebundener Halogene (AOX)

Qualité de l'eau - Dosage des halogenes des composés organiques adsorbables (AOX)

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ICS:

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| 13.060.50 | Preiskava vode na kemične snovi | Examination of water for chemical substances |
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EUROPEAN STANDARD

EN 1485

NORME EUROPÉENNE

EUROPÄISCHE NORM

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ICS 13.060.40

Descriptors: water, quality, water tests, chemical analysis, determination of content, bromine organic compounds, chlorine organic compounds, halogens

English version

Water quality - Determination of adsorbable organically bound halogens (AOX)

Qualité de l'eau - Dosage des halogènes des composés organiques adsorbables (AOX)

Wasserbeschaffenheit - Bestimmung adsorbierbarer organisch gebundener Halogene (AOX)

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Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Foreword

This European Standard has been prepared by the Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 1997, and conflicting national standards shall be withdrawn at the latest by March 1997.

This European Standard contains three informative annexes.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

It is absolutely essential that tests conducted according to this standard are carried out by suitably qualified staff.

AOX is an analytical convention, the result is a parameter used for water quality control purposes. It represents the sum of organically bound chlorine, bromine and iodine (but not fluorine) which can be adsorbed on activated carbon under specified conditions and, if the sample is not filtered, includes that associated with suspended matter.

1 Scope

This European Standard specifies a method for the direct determination of an amount of more than 10 µg/l in water of organically bound chlorine, bromine and iodine (expressed as chloride) adsorbable on activated carbon.

The concentration of inorganic chloride ions in the test sample (see clause 8) needs to be less than 1 g/l. Samples with higher concentrations need to be diluted prior to analysis.

For samples containing suspended solids, halogens adsorbed onto the solid matter are also included. Filtration of the sample before analysis enables the determination of dissolved and particulate AOX to be carried out.

NOTE: The recovery of some polar and hydrophilic compounds, such as monochloroacetic acid, is incomplete.

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1.1 Interferences

1.1.1 High AOX values can result from the presence of active chlorine. Reactions of this oxidizing agent with organic substances in the sample and with the activated carbon can be prevented by the addition of sodium sulfite, immediately after sampling.

1.1.2 Some inorganic bromine and iodine compounds are irreversibly bound to activated carbon causing positive bias. These interferences can be diminished by the addition of sodium sulfite.

1.1.3 Organic bromine and iodine compounds may, during combustion, decompose to elemental bromine or iodine respectively and this can yield higher oxidation states of these elements. These fractions of AOX may be incompletely determined, thus leading to negative bias.

1.1.4 Insoluble inorganic halides can cause positive bias.

1.1.5 Samples containing living cells (for example microorganisms or algae) may give rise to high results because of their chloride content. In these cases the sample is not analyzed until at least 8 h after acidification.

1.1.6 For samples with high chloride concentrations (approximately 1 g/l) the shaking procedure (see 8.2.1) can result in higher interferences (positive bias, see 9.2) than the column procedure (see 8.2.2).



2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated reference, subsequent amendment to or revisions of any of these publications apply to this European standard only when incorporated in it by amendment or revision. For undated reference the latest edition of the publication referred to applies.

EN 25667-1 : 1993
Water quality – Sampling – Part 1: Guidance on the design of sampling programmes (ISO 5667-1 : 1991)

EN 25667-2 : 1993
Water quality – Sampling – Part 2: Guidance on sampling techniques (ISO 5667-2 : 1984)

EN ISO 5667-3 : 1995
Water quality – Sampling – Part 3: Guidance on the preservation and handling of samples

prEN 1484 : 1994
Water quality – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

EN ISO 3696 : 1995
Water for laboratory use – Specification and test methods

3 Definitions

For the purpose of this European Standard, the following definitions apply:

3.1 Adsorbable organically bound halogens (AOX)

The equivalent amount of chlorine, bromine, and iodine contained in organic compounds, expressed as chloride when determined according to this European standard.

3.2 Dissolved organic carbon (DOC)

The amount of organic carbon present in a water sample after filtration through a membrane filter of pore size 0,45 μm .

4 Principle

Acidification of the water sample with nitric acid. Adsorption onto activated carbon of organic compounds contained in the sample, either by a shaking procedure or by column adsorption. Displacement of inorganic halides by rinsing the activated carbon with acidified sodium nitrate solution. Combustion of the loaded carbon in an oxygen stream. Absorption of the hydrogen halides followed by determination of the halide ions by an argentometric titration, such as microcoulometry. Expression of the result as the mass concentration of chloride.

5 Reagents

Use only reagents of recognized analytical grade and water grade 1 in accordance with EN ISO 3696. The purity of water, reagents and gases shall be confirmed.

The AOX content shall be negligibly low when compared with the lowest AOX content to be determined. The overall AOX content of water, chemicals, and gases can be checked by measuring the total blank (see 8.5).

5.1 Activated carbon

For the shaking procedure, use an activated carbon of about 10 μm to 50 μm grain size. For the column adsorption, use a grain size distribution of 50 μm to 150 μm .

For the storage of activated carbon, see Annex A.

NOTE: Several methods can be used for the determination of the adsorption capacity. One of these methods is described in [1]. The iodine number gives an indication of the adsorption capacity of the activated carbon. The iodine number determined in accordance with the method specified in [1], should be > 1050 .

The blank value of the washed activated carbon shall be less than 15 μg of chloride equivalent per gram of activated carbon.

5.2 Nitric acid, HNO_3 , $\rho = 1,4$ g/ml, 65 % (m/m) solution.

5.3 Hydrochloric acid, $c(\text{HCl}) = 0,100$ mol/l

The molarity shall precisely be known, since the acid is used for checking the microtitration (see 8.4.1).

5.4 Sulfuric acid, H_2SO_4 , $\rho = 1,84$ g/ml.

5.5 Gases for combustion, for example oxygen (O_2), or a mixture of oxygen and an inert gas.

5.6 Nitrate, stock solution, $c(\text{NaNO}_3) = 0,2$ mol/l

– Dissolve 17 g of sodium nitrate (NaNO_3) in water in a 1000 ml volumetric flask, add 1,4 ml of nitric acid (see 5.2), and make up to volume with water.

5.7 Nitrate washing solution, $c(\text{NaNO}_3) = 0,01$ mol/l

– Pipette 50 ml of the nitrate stock solution (see 5.6) in a 1000 ml volumetric flask, and make up to volume with water.

5.8 Sodium sulfite solution, $c(\text{Na}_2\text{SO}_3) = 1$ mol/l

– Dissolve 126 g Na_2SO_3 in water in a 1000 ml volumetric flask and make up to volume with water.

5.9 4-Chlorophenol, stock solution, AOX = 200 mg/l

– Dissolve 72,5 mg of 4-chlorophenol ($\text{C}_6\text{H}_5\text{ClO}$) in water in a 100 ml volumetric flask and make up to volume with water.

5.10 4-Chlorophenol, working solution, AOX = 1 mg/l

– Pipette 5 ml of 4-chlorophenol, stock solution, (see 5.9) into a 1000 ml volumetric flask, and make up to volume with water.

5.11 2-Chlorobenzoic acid, stock solution, AOX = 250 mg/l

– Dissolve 110,4 mg of 2-chlorobenzoic acid ($\text{ClC}_6\text{H}_4\text{COOH}$) in water in a 100 ml volumetric flask and make up to volume with water.

The dissolution of 2-chlorobenzoic acid is very slow. It is recommended to prepare this solution the day before using it.

5.12 2-Chlorobenzoic acid, working solution, AOX = 1 mg/l

– Pipette 4 ml of 2-chlorobenzoic acid, stock solution (see 5.11), into a 1000 ml volumetric flask, and make up to volume with water.

The stock solutions (see 5.9 and 5.11) may be stored for at least 1 month and the working solutions (see 5.10 and 5.12) for 1 week at 4 °C in glass bottles.

5.13 Standard solutions for the checks on the overall procedure (8.4.2)

– Pipette 1 ml, 5 ml, 10 ml, 20 ml, and 25 ml of the working solutions (see 5.10 or 5.12) into five separate 100 ml volumetric flasks, and make up to volume with water.

The AOX mass concentration of these solutions is 10 $\mu\text{g/l}$, 50 $\mu\text{g/l}$, 100 $\mu\text{g/l}$, 200 $\mu\text{g/l}$ and 250 $\mu\text{g/l}$ respectively.

The standard solutions shall be prepared daily.

6 Apparatus

6.1 Apparatus for the combustion and detection

6.1.1 Combustion apparatus

A furnace, capable of being heated to at least 950 °C, equipped with a quartz tube approximately 30 cm long with an internal diameter of between 2 cm and 4 cm (see figure 1 in annex B).

6.1.2 Quartz container, to fit in the quartz tube

6.1.3 Argentometric measuring device for determining halide concentrations, for example a microcoulometer, capable of determining at least 1 µg chloride with a coefficient of variation (repeatability) of less than 10 %, or an equivalent device to determine chloride ions.

6.1.4 Absorber, filled with sulfuric acid (see 5.4), to dry the gas stream and designed so that the acid does not backflush into the furnace.

6.1.5 Syringe, to pipette volumes of 1 µl to 10 µl of hydrochloric acid (see 5.3).

6.2 Adsorption unit

6.2.1 Adsorption unit for the shaking procedure (8.2.1)

6.2.1.1 Filtration apparatus, for example with a funnel capacity of 0.15 l and filter diameter 25 mm.

6.2.1.2 Polycarbonate membrane filter, for example with internal diameter of 25 mm and a pore size of 0,45 µm, or any equivalent filtration material, such as a quartz filter.

6.2.1.3 Conical flask (Erlenmeyer flask)

6.2.1.4 Mechanical shaker for the flasks described in 6.2.1.3 above, equipped for example with a carrier plate.

6.2.2 Adsorption unit for the column adsorption (8.2.2)

A suitable pump, for example a piston pump, with PTFE hose (PTFE = polytetrafluoroethylene) and two adsorption columns, arranged in series and vertically mounted, with an internal diameter of approximately 3 mm, length 40 mm to 50 mm, packed with approximately 50 mg of activated carbon, shall be installed. Other dimensions of the columns are permissible. Suspended matter may tend to clog the columns. To prevent this an in-line pre-filter, for example packed with ceramic wool (6.2.3) as filtration material, connected to the inlet, is necessary.

6.2.3 Ceramic wool or equivalent material to retain the activated carbon in the columns.

7 Sampling and sample pretreatment

– Use glass or plastics vessels and an appropriate closure material such as PTFE. Verify that losses of organically bound halogens or contamination do not interfere.

Where lower concentrations of organic halogen compounds (e.g. if AOX < 50 µg/l) are anticipated, glass containers are preferable.

– Collect the samples taking into account the particular properties of the matrix ensuring that no losses of the target analytes occur.

– If the samples are suspected of containing oxidizing agents, immediately add at the time of sampling up to 10 ml of sodium sulfite solution (5.8) per litre of sample.

– To test samples for the presence of active chlorine before or after the addition of sodium sulfite (see 5.8) on a separate sample aliquot apply the following procedure. Transfer some millilitres of the acidified sample into a test-tube. Dissolve a few crystals of potassium iodide (KI) in the sample and add a few drops of a 1 % starch solution. A blue colour indicates the presence of active chlorine. Other oxidants with sufficient oxidation potentials may give the same reaction.

- Add 2 ml of nitric acid (see 5.2) per litre of sample and completely fill the sample bottle leaving no air gap, if necessary (see 1.1.5), allow the sample to stand for 8 h. Usually the quantity of the added acid is sufficient to yield a pH < 2. It may be necessary to add more acid to attain this pH.
- Analyze the water sample as soon as possible after sampling, or, in the presence of living cells (see 1.1.5) 8 h after sampling. If this is not possible and storage is essential, store the acidified sample at 4°C or deep freeze it.
- Prior to analysis allow the sample to equilibrate to room temperature.

NOTE: For samples containing volatile organic halogen compounds, for example chlorinated solvents, it is recommended that analysis is started within 24 h after sampling. A maximum storage time is not given since individual circumstances will dictate the requirements.

8 Procedure

The test sample taken for analysis shall ideally have an AOX value within the optimal working range of the instrument, which is generally between 10 µg/l to 300 µg/l. The chloride concentration shall not exceed 1 g/l. It may be necessary to dilute the sample with acidified water to achieve a pH < 2 before commencing the analysis.

- When it is necessary to dilute, do not use less than 5 ml of the original sample. Note the dilution factor (final volume divided by the original volume). If the dilution factor is greater than 10, dilute in at least two steps.

8.1 Homogenization

- Ensure that the sample is homogenized by stirring or shaking the sample in the sampling bottle until complete mixing can be observed.
- Take a homogenized test sample of 100 ml.

If the sample cannot be completely homogenized, consider filtering prior to any other sample pretreatment. In such cases only the soluble AOX components of the sample will be determined.

8.2 Adsorption

8.2.1 Shaking Procedure

- Transfer the test sample (see 8.1) into a stoppered conical flask (see 6.2.1.3), the nominal capacity of which shall not exceed 250 ml in order to restrict the headspace.
- Add 5 ml of nitrate stock solution (see 5.6) to the flask and ensure that the pH is less than 2.
- Add 50 mg of activated carbon (see 5.1) stopper the flask and shake the suspension for 1 h.
- Filter the suspension through a filtration system (see 6.2.1.1). If difficulties arise with the filtration, dilute the subsample and apply pressure filtration.
- Wash the filter cake with approximately 25 ml of nitrate washing solution (see 5.7), applying the solution in several portions (see note 2).
- Place the moist filter and the filter cake into the quartz combustion container (see 6.1.2) and proceed according to 8.3.

To check the completeness of the adsorption use

- either two separate test sample aliquots and/or dilution steps or
- add another 50 mg of activated carbon after completion of the first adsorption step.

Note 1: In the first two cases, the AOX values of both measurements should not deviate from each other by more than 10 %. In the third case the AOX value obtained from the second adsorption step should not exceed 10 % of the AOX value from the first step. The adsorption can also be regarded as complete if the DOC (see 3.2) of the test sample does not exceed 10 mg/l.

NOTE 2: It is essential that the filter cake is not sucked to dryness, since this may lead to positive bias, for example caused by contaminated laboratory air.

NOTE 3: In the case of high chloride concentrations, which cannot be reduced by dilution of the sample due to corresponding reductions in the AOX value (see clause 8), it is recommended to use the column procedure (see 8.2.2).

8.2.2 Column Procedure

- Add 5 ml of nitrate solution (see 5.6) to the test sample (see 8.1).
- Ensure that the pH is below 2, if not, add more nitric acid (see 5.2).
- Pass the sample through the adsorption columns arranged in series (see 6.2.2) at a flow rate of 3 ml/min.
- Wash the columns with approximately 25 ml of the nitrate washing solution (see 5.7), at a flow rate of 3 ml/min.
- Separately combust the moist activated carbon and the ceramic wool (used for activated carbon retainment in the column and prefiltration of the test sample) from each adsorption column, and also the pre-filter, if used (see 6.2.2) as described in 8.3.
- Use the AOX results of both columns to check the completeness of the adsorption, (see note 1 below).

NOTE 1: The AOX value obtained from the second adsorption column should not exceed 10 % of the AOX value from the first column, otherwise it is recommended for the determination to be repeated; it may be necessary for the sample to be diluted or to use additional adsorption steps. If the DOC of the sample does not exceed 10 mg/l a complete adsorption can be assumed. In specific cases (e.g. surface water) joint combustion of the loaded activated carbon in both columns is recommended.

NOTE 2: Rinsing with volumes > 25 ml nitrate washing solution (see 5.7) reduces chloride interferences, but reduces the AOX recovery as well. Appropriate notes should be made in the laboratory report indicating the use of this modification to the procedure.

NOTE 3: If particulate matter is to be included in the determination, it is essential that the solid material remains on the top of the column.

8.3 Combustion

The temperature in the combustion chamber (see 6.1.1) shall be at least 950 °C; select the other operating parameters in accordance with the manufacturer's instructions.

- Connect the gas supply to the combustion tube and the combustion tube to the absorber (see 6.1.4).
- Do not allow back-siphoning of the sulfuric acid into the combustion tube; this can happen if a drop in temperature or pressure occurs.
- Adjust the gas flow (see 5.5) to approximately 150 ml/min.
- Introduce the quartz container (see 6.1.2) into the heated zone of the tube, following the manufacturer's instructions.

NOTE: A number of experimental variables, for example the amount of activated carbon applied, the test sample volume (see 8.1), the dimensions of the furnace, residence time, combustion temperature, and the adjustment of the gas flow (see 5.5 and 8.3) will depend on the type of apparatus and may also affect the result.

8.4 Operational tests of the method

8.4.1 Checks on the instrumentation used to determine halide concentrations

In the case of microcoulometric determination, check the instrument daily within the relevant working range, using at least one test solution as follows.

- Inject directly with a syringe (see 6.1.5) a volume within the range of 5 μ l to 8 μ l of the hydrochloric acid solution (see 5.3) into the titration cell.
- Measure the quantity of charge transferred in this test.