INTERNATIONAL
STANDARD

ISO
9562

Third edition
2004-09-15

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

Qualité de l'eau — Dosage des composés organiques halogénés adsorbables (AOX)

Reference number
ISO 9562:2004(E)

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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 9562 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This third edition cancels and replaces the second edition (ISO 9562:1998), which has been technically revised.

Introduction

Adsorbable organically bound halogens (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) that can be adsorbed on activated carbon under specified conditions and, if the sample is not filtered, includes that associated with suspended matter.

The user should be aware that particular problems could require the specification of additional marginal conditions.

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

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International 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 International Standard be carried out by suitably qualified staff.

1 Scope

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

This method is applicable to test samples (see 9.2) with concentrations of inorganic chloride ions of less than 1 g/l. Samples with higher concentrations are diluted prior to analysis.

This method is also applicable to samples containing suspended solids where halogens are adsorbed onto the solid matter (e.g. insoluble halides). Filtration of the sample before analysis allows the separate determination of dissolved and particulate adsorbable organically bound halogens (AOX).

Filtered samples with high inorganic chloride content can be analysed by a modified method [dissolved adsorbable organically bound halogens after solid phase extraction in waters with high salt content (SPE-AOX)] (see Annex A). However, results obtained by this modified method can differ significantly from those of the required method.

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 1773:1997, *Laboratory glassware — Narrow-necked boiling flasks*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

3.1
adsorbable organically bound halogens
AOX
equivalent amount of chlorine, bromine, and iodine contained in organic compounds, expressed as chloride when determined according to this International Standard

3.2
dissolved organic carbon
DOC
amount of organically bound carbon present in water originating from compounds passing through a membrane filter of 0,45 µm pore size and including cyanate and thiocyanate

4 Interferences

4.1 High AOX values can result from the presence of active chlorine and of some inorganic bromine and iodine compounds, irreversibly bound to activated carbon. Reactions of these oxidizing agents with organic substances in the sample and with the activated carbon can be prevented by the addition of sodium sulfite, immediately after sampling.

4.2 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.

4.3 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 analysed until at least 8 h after acidification.

4.4 For samples with high chloride concentrations (approximately 1 g/l), the shaking procedure (9.3.2) can result in higher interferences than the column procedure (9.3.4).

4.5 Alcohols, aromatic compounds, or carboxylic acids may give rise to negative bias (e.g. in case of DOC values $>$ 100 mg/l).

4.6 For samples containing suspended solids, the stirring method (9.3.3) may lead to an insufficient covering of the particles. If the particles contain substances contributing to the AOX, the shaking or column method is recommended.

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

5 Principle

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

6 Reagents

Use only reagents of recognized analytical grade. The purity of water, reagents and gases shall be confirmed.

The AOX content shall be negligible 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 (10.2).

6.1 **Water**, Grade 1 as specified in ISO 3696:1987.

6.2 **Activated carbon**, the handling of which is given in Annex B, for one of three procedures listed in 6.2.1 to 6.2.3.

Several methods may be applied to determine the adsorption capacity. One of these methods is described in reference [1]. The iodine number gives an indication of the activated carbon adsorption capacity. According to the method given in reference [1], the iodine numbers shall be $> 1\,050$.

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

6.2.1 Activated carbon for the shaking procedure, with a grain size of about 10 µm to 50 µm.

6.2.2 Activated carbon fleeces for the stirring procedure, are commercially available[1].

6.2.3 Activated carbon for the column procedure, with a grain size of about 50 µm to 150 µm.

6.3 Nitric acid, HNO_3.

6.3.1 Nitric acid, **concentrated**, $\rho(HNO_3) = 1{,}4$ g/ml, $w(HNO_3) = 65$ %.

6.3.2 Nitric acid, dilute, $c(HNO_3) = 0{,}02$ mol/l.

6.4 Hydrochloric acid, $c(HCl) = 0{,}010$ mol/l.

The molarity shall be known precisely, since the acid is used for checking the microtitration (9.5.1).

6.5 Sulfuric acid, H_2SO_4, $\rho(H_2SO_4) = 1{,}84$ g/ml.

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

6.7 Nitrate, stock solution, $c(NaNO_3) = 0{,}2$ mol/l.

Dissolve 17 g of sodium nitrate ($NaNO_3$) in water (6.1) in a 1 000 ml volumetric flask, add 25 ml of concentrated HNO_3 (6.3.1), and make up to volume with water (6.1).

If stored in a brown glass bottle, the solution is stable for three months.

6.8 Nitrate washing solution, $c(NaNO_3) = 0{,}01$ mol/l, pH $\approx 1{,}7$.

Pipette 50 ml of the nitrate stock solution (6.7) in a 1 000 ml volumetric flask, and make up to volume with water (6.1).

If stored in a brown glass bottle, the solution is stable for one month.

6.9 Sodium sulfite solution, $c(Na_2SO_3) = 1$ mol/l.

Dissolve 126 g of Na_2SO_3 in water (6.1) in a 1 000 ml volumetric flask and make up to volume with water (6.1).

The solution is stable for one month if stored at 2 °C to 8 °C.

6.10 4-Chlorophenol, **stock solution**, $\rho_{Cl}(AOX) = 200$ mg/l.

Dissolve 72,5 mg of 4-chlorophenol (C_6H_5ClO) in water (6.1) in a 100 ml volumetric flask and make up to volume with water (6.1).

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[1] A suitable product available commercially can be obtained from Normenausschuss Wasserwesen (NAW) im DIN Deutsches Institut für Normung e. V., 10772 Berlin. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

For security reasons, it is advisable to use commercially available solutions.

This stock solution may be stored one month at 2 °C to 8 °C in a glass bottle.

6.11 4-Chlorophenol, working solution, ρ_{Cl}(AOX) = 1 mg/l.

Pipette 5 ml of 4-chlorophenol, stock solution (6.10), into a 1 000 ml volumetric flask, and make up to volume with water (6.1).

This working solution may be stored one week at 2 °C to 8 °C in a glass bottle.

6.12 2-Chlorobenzoic acid, stock solution, ρ_{Cl}(AOX) = 250 mg/l.

Dissolve 110,4 mg of 2-chlorobenzoic acid (ClC_6H_4COOH) in water in a 100 ml volumetric flask and make up to volume with water (6.1).

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

This stock solution may be stored for one month at 2 °C to 8 °C in a glass bottle.

6.13 2-Chlorobenzoic acid, working solution, ρ_{Cl}(AOX) = 1 mg/l.

Pipette 4 ml of 2-chlorobenzoic acid, stock solution (6.12), into a 1 000 ml volumetric flask, and make up to volume with water (6.1).

This working solution may be stored 1 week at 2 °C to 8 °C in a glass bottle.

6.14 Standard solutions for the checks, on the overall procedure (9.5.2).

Pipette, for example, 1 ml, 5 ml, 10 ml, 20 ml, and 25 ml of the working solutions (6.11 or 6.13) into five separate 100 ml volumetric flasks, and make up to volume with water (6.1).

The AOX mass concentration of these solutions is 10 µg/l, 50 µg/l, 100 µg/l, 200 µg/l and 250 µg/l respectively.

The concentration of the solutions should be chosen in such a way that the total working range is covered.

Prepare fresh standard solutions on the day of use.

6.15 Potassium iodide (KI).

6.16 Starch solution, having a mass fraction of 1 %.

7 Apparatus

7.1 Activated carbon adsorption apparatus.

7.1.1 Adsorption apparatus for the shaking procedure (9.3.2).

7.1.1.1 Filtration apparatus, for example with filter funnel of capacity of V = 0,15 l and filter diameter of 25 mm.

7.1.1.2 Polycarbonate membrane filter, for example with diameter of 25 mm and pore width of 0,45 µm or equivalent filter material.

7.1.1.3 Conical flask, 250 ml, in accordance with ISO 1773.

7.1.1.4 Mechanical shaking device for the flasks, specified in 7.1.1.3, for example with carrier plate.

7.1.2 Adsorption apparatus for the stirring method (9.3.3)

7.1.2.1 Conical flask, 100 ml, in accordance with ISO 1773.

7.1.2.2 Attachment device for the activated carbon fleece, e.g. coil, attached to the stopper.

7.1.2.3 Activated carbon fleece, for example round discs, 13 mm × 3 mm, activated carbon fibre (100 % carbon), specific surface 1 600 m^2/g, mass 25 mg (for each measurement, two fleeces with a total mass of 50 mg of activated carbon are used).

7.1.2.4 Rinsing device, e.g. magnetic stirrer with cylindrical glass filter funnel for fixation of the activated carbon fleece.

7.1.3 Adsorption apparatus for the column procedure (9.3.4).

Suitable pump, e.g. piston pump with polytetrafluoroethene (PTFE) tube and with adsorption tubes, inner diameter about 3 mm, length 40 mm to 50 mm, attached vertically one behind the other. Other column dimensions are acceptable. Each tube should be filled with about 50 mg of activated carbon. Add the sample from the top of the column and transport it through the column using overpressure.

7.1.3.1 Ceramic wool, or equally suitable material, free from halogens, for fixation of the activated carbon in the columns.

7.2 Apparatus for combustion and detection.

7.2.1 Combustion apparatus, consisting of a furnace, capable of being heated at least to 950 °C, equipped with a quartz tube, with an inner diameter of 2 cm to 4 cm and length of about 30 cm (see example Figure 1), of which both vertical and horizontal combustion tubes are common.

7.2.2 Quartz container, suitable for the quartz tube.

7.2.3 Argentometric measurement device, for determination of halide concentrations, usually microcoulometer, suitable for the determination of 1 µg of chloride (absolute) with a coefficient of variation of 10 % (repeatability), or similar device (e.g. titration with a diluted $AgNO_3$ solution) for the determination of chloride ions.

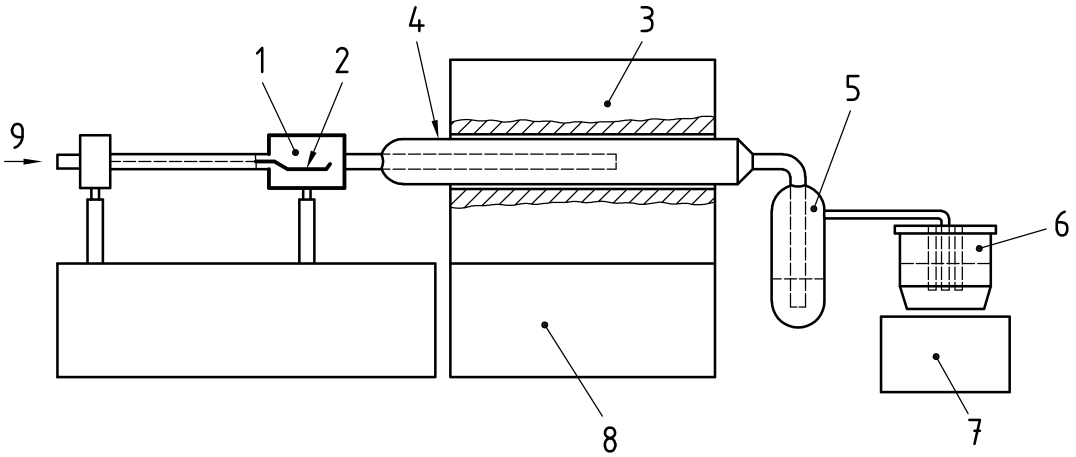
7.2.4 Absorber, filled with sulfuric acid (6.5) for gas drying. The acid shall not backflush into the oven. The acid shall be exchanged if its volume has increased by more than 20 %.

7.2.5 Syringe, suitable for pipetting 10 µl to 100 µl of hydrochloric acid (6.4).

7.3 Additional apparatus.

7.3.1 Measuring flask, 1 000 ml, e.g. ISO 1042 - A 1 000 - C.

7.3.2 Flat bottomed sampling bottles, preferably brown glass, 1 000 ml.



Key

1 sample inlet for AOX
2 AOX sample
3 furnace
4 combustion tube
5 absorber filled with sulfuric acid (6.5)
6 titration cell
7 stirrer
8 control device for temperature, gas flow
9 combustion gas inlet

Figure 1 — Schematic diagram of an AOX apparatus (example)

8 Sampling and sample pre-treatment

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

Where lower concentrations of organic halogen compounds (e.g. if $\rho_{\mathrm{Cl}}(\mathrm{AOX}) < 50$ 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 (6.9) per litre of sample.

To test samples for the presence of active chlorine before or after the addition of sodium sulfite (6.9), apply the following procedure on a separate sample aliquot.

a) Transfer a few millilitres of the acidified sample into a test tube. Dissolve a few crystals of potassium iodide (KI) (6.15) in the sample and add a few drops of a 1 % starch solution (6.16). A blue colour indicates the presence of active chlorine. Other oxidants with sufficient oxidation potentials may give the same reaction.

b) Add 2 ml of concentrated HNO_3 (6.3.1) per litre of sample and completely fill the sample bottle leaving no air gap, if necessary (see 4.3), 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 concentrated or dilute HNO_3 (6.3.1 or 6.3.2) to attain this pH.

c) Analyse the water sample as soon as possible after sampling, or, in the presence of living cells (4.3) 8 h after sampling. If this is not possible and storage is essential, store the acidified sample at 4 °C or deep freeze it.

d) Prior to analysis, allow the sample to equilibrate to room temperature.

If volatile organic halogen compounds, for example chlorinated solvents, are expected, it is recommended to start analysis within 24 h after sampling. A maximum storage time is not given since individual circumstances will dictate the requirements.

9 Procedure

9.1 General

Prior to analysis, it is recommended to determine the limit of quantification from a blank measurement (10.2) as a rough estimation. According to the result, the limit of determination may be equalized to the nine-fold value of the standard deviation of the blank mean.

The test sample taken for analysis shall have a ρ_{Cl}(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 dilute HNO_3 (6.3.2) to achieve a $\mathrm{pH} < 2$ before starting the analysis.

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

Samples with higher chloride concentrations may be analysed by using the modified method described in Annex A.

NOTE 1 In Clause 9 only the microcoulometric procedure is described.

NOTE 2 A complete absorption can be assumed if the COD value is below 10 mg/l.

9.2 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.

Together with the test samples, analyse the blanks (9.4).

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. If the sample has been filtered, it should be clearly reported in the test report that this result represents only dissolved AOX.

9.3 Adsorption on activated carbon

9.3.1 General

Prior to adsorption on activated carbon, add 5 ml of nitrate stock solution (6.7) to the test sample (9.2).

9.3.2 Shaking procedure

Transfer the treated test sample (9.3.1) into a stoppered conical flask (7.1.1.3), its nominal capacity shall not exceed 250 ml in order to restrict the headspace.

Add 50 mg of activated carbon (6.2), stopper the flask and shake the suspension for 1 h.

Filter the suspension through a filtration apparatus (7.1.1.1). If difficulties arise with the filtration, dilute the sub-sample and apply pressure filtration.

Wash the filter cake with approximately 25 ml of nitrate washing solution (6.8), applying the solution in several portions. Rinsing with volumes > 25 ml nitrate washing solution (6.8) reduces chloride interferences, but reduces the AOX recovery as well. Appropriate information should be provided in the laboratory report indicating the use of this modification to the procedure.

Do not evacuate to dryness because this may lead to elevated results, e.g. from contaminated laboratory air.

Place the moist filter and the filter cake into the quartz container (7.2.2) and proceed according to 9.6.

Chloride concentrations in the range of 500 mg/l to 1 000 mg/l cannot be reduced by dilution of the sample due to corresponding reductions in the AOX value (see 9.1). In this case, it is recommended to use the column procedure (9.3.4).

9.3.3 Stirring procedure (Carbodisc method)

Carry out the adsorption step sequentially, e.g. by applying two activated carbon fleeces.

Transfer the treated test sample from 9.3.1 to a 100 ml conical flask (7.1.2.1).

Insert a magnetic stirrer bar to the conical flask.

Adjust the activated carbon fleece in the attachment device (7.1.2.2) and dip it into the sample. Close the flask firmly with the stopper of the attachment device. Stir the sample for 30 min at a rate of 750 min^{-1}.

Withdraw the fleece and spread it on the bottom of the rinsing device (7.1.2.4). Retain the sample, and rinse the fleece in several portions with 12,5 ml of the nitrate washing solution (6.8). Discard the rinsing solution.

Repeat the procedure with the retained sample and a second activated carbon fleece.

Proceed according to 9.6.

9.3.4 Column procedure

Run the treated test sample obtained in 9.3.1 through two adsorption columns (7.1.3), vertically mounted in series, at a flow rate of 3 ml/min.

Rinse the columns with 25 ml of nitrate washing solution (6.8) at a flow rate of 3 ml/min.

Proceed according to 9.6.

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

Rinsing with volumes > 25 ml nitrate washing solution (6.8) reduces chloride interferences, but reduces the AOX recovery as well. Appropriate information should be provided in the laboratory report indicating the use of this modification to the procedure.

9.4 Blank determination

Make a blank determination using 100 ml of dilute HNO_3 (6.3.2) instead of the sample and analyse it in the same way as stated for the sample.

Record the measured values obtained from argentometric measurement device, expressed in Coulomb (C), Q_0, for the blanks. Calculate the value of the ρ_{Cl}(blank) as specified in 10.1.

The calculated AOX value for the total blank, ρ_{Cl}(blank), shall not exceed 30 µg/l for a test sample volume of 100 ml. If this value is exceeded, check the adsorption steps, the combustion and the argentometric titration separately.

In practice, calculated AOX values for blanks ρ_{Cl}(blank < 10 µg/l) are easily obtainable.

Considerable contamination of the laboratory air can arise from laboratory chemicals or other sources.

If the test sample (9.2) contains both a low ρ_{Cl}(AOX) value and a chloride concentration of approximately 1 g/l, a significant positive bias may arise. In these cases, it is recommended to spike the blank with the same chloride concentration as contained in the test sample. By this means any bias $\leqslant$ 5 %, caused by inorganic chloride can be compensated.

9.5 Preliminary tests and check tests

9.5.1 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.

a) Using a syringe (7.2.5), directly inject a volume between 50 µl and 80 µl of the hydrochloric acid solution (6.4) into the titration cell.

b) Measure the quantity of charge transferred in this test.

Coulometry theory assumes a 100 % current yield. Obtain the test factor, a, by using Equation (1):

$$Q = a \times Q_{\mathrm{t}} \tag{1}$$

where

Q is the measured quantity of charge, expressed in Coulomb (C), for the hydrochloric acid sample;

Q_{t} is the theoretical quantity of charge, expressed in Coulomb (C), for the hydrochloric acid sample;

a is the test factor.

Obtain the theoretical quantity of charge, Q_{t} using Equation (2):

$$Q_{\mathrm{t}} = V \times c_{\mathrm{Cl}} \times F \tag{2}$$

where

V is the volume, expressed in litres, of the hydrochloric acid solution;

c_{Cl} is the chloride concentration, expressed in moles per litre, of the hydrochloric acid solution;

F is the Faraday constant (F = 96 484,56 C/mol).

The measuring device is suitable for the analysis if the test factor, a, is in the range of 0,97 to 1,03.

9.5.2 Checks on the overall procedure

9.5.2.1 Daily check

Check the entire procedure daily by running a standard solution (6.14) with a concentration in the middle of the working range of the instrument. Calculate the ρ_{Cl}(AOX) values as specified in 10.1.

The ρ_{Cl}(AOX) value thus obtained and the theoretical value shall not deviate by more than 10 % (recovery 90 % to 110 %).

9.5.2.2 Initial check

An initial check is necessary when this method is first introduced into the laboratory if

- essential parts of the apparatus are changed,
- on the daily check (9.5.2.1) a deviation of $>$ 10 % is obtained, or
- different or new staff are employed to carry out the determinations.

This initial check is carried out as follows.

a) Analyse a blank sample (9.4) and at least five standard solutions (6.14) and compare the measured results, calculated as specified in 10.1, with the nominal values.

b) Test the correlation of the measured values by comparison with the nominal AOX values (recovery function).

The result is acceptable if the correlation coefficient is $\geqslant$ 0,999 and the slope of the recovery function is within the range of 0,95 to 1,05. In addition, the data can be evaluated graphically which will identify any outliers present.

High variances or non-linearity of the recovery function may cause unsatisfactory results.

9.6 Combustion and determination of the halide ions

The temperature in the combustion apparatus shall be at least 950 °C (7.2.1) whereas the remaining parameters are chosen according to the information given by the manufacturer.

Connect the gas supply to the combustion tube and the combustion tube to the absorber (7.2.4).

WARNING — Avoid backflush of sulfuric acid into the combustion tube. This may be caused by temperature or pressure depression.

Adjust the gas flow rate to about 150 ml/min.

Transfer the wet filter together with the filter cake obtained using the shaking procedure (9.3.2), the fleeces obtained using the stirring procedure (9.3.3), the wet activated carbon and the ceramic wool from each column or using the column procedure (9.3.4) to the quartz container (7.2.2).

Introduce the quartz container (7.2.2) into the heated zone of the combustion apparatus (7.2.1) equipped with the argentometric measurement device (7.2.3) following the manufacturer's instructions.

Record the measured values obtained from argentometric measurement device, expressed in Coulomb (C), Q_{S}, for the test samples (9.2) and proceed to 10.1.

NOTE A number of experimental variables, for example the amount of activated carbon applied, the test sample volume (9.2), the dimensions of the furnace, residence time, combustion temperature and the adjustment of the gas flow (6.6) will depend on the type of apparatus and can also affect the result.

10 Calculation

10.1 Mass concentration of adsorbable organically bound halogens [ρ_{Cl}(AOX)]

Calculate the mass concentration of adsorbable organically bound halogens using Equation (3):

$$\rho_{\mathrm{Cl}}(\mathrm{AOX}) = \frac{(Q_{\mathrm{s}} - Q_0)M \times 1\ 000}{V \times F} = \rho_{\mathrm{Cl}}(\mathrm{sample}) - \rho_{\mathrm{Cl}}(\mathrm{blank}) \qquad (3)$$

where

ρ_{Cl}(AOX)	is the calculated mass concentration of adsorbable organically bound halogens, expressed as chloride, in milligrams per litre (mg/l) or micrograms per litre (µg/l);
ρ_{Cl}(sample)	is the uncorrected ρ_{Cl}(AOX) value, expressed in the same units as ρ_{Cl}(AOX), for the test sample;
ρ_{Cl}(blank)	is the ρ_{Cl}(AOX) value, expressed in the same units as ρ_{Cl}(AOX), for the blank;
M	is the molar mass of chloride, $M = 35{,}45 \times 10^6$ µg/mol, if the result is expressed in micrograms per litre (µg/l) and $M = 35{,}45 \times 10^3$ mg/mol, if the result is expressed in milligrams per litre (mg/l);
V	is the volume, expressed in millilitres (ml), of the original sample contained in the test sample according to 9.2;
F	is the Faraday constant, as defined in Equation (2).

The symbols Q_0 and Q_{s} are defined in 9.4 and 9.6.

The results shall be expressed in µg/l or mg/l chloride to two significant figures.

EXAMPLES

ρ_{Cl}(AOX) = 74 µg/l

ρ_{Cl}(AOX) = 6,2 mg/l

10.2 Checking of the completeness of the total adsorption

Using two different test sample volumes and/or dilution steps, the ρ_{Cl}(AOX) values obtained shall not differ by more than 10 %. In the case of ρ_{Cl}(AOX) values $<$ 100 µg/l, the absolute difference of both results shall not exceed 10 µg/l.

11 Precision

Annex C gives the statistical and other data results, obtained by an interlaboratory test with 96 participants, carried out by the CEN in October 1992.

12 Test report

The following information shall be given in the test report.

a) reference to this International Standard (ISO 9562:2004);

b) precise identification of the water sample;

c) pre-treatment, adsorption, combustion, and determination methods used;

d) results of the test in accordance with Clause 10;

e) any facts, which may have influenced the result.

Annex A
(informative)

Determination of dissolved adsorbable organically bound halogens after solid phase extraction (SPE-AOX) in waters with high salt content

A.1 General

For filtered samples with higher concentrations of inorganic chloride (up to 100 g/l) and higher DOC contents (up to 1 000 mg/l) this modified AOX method can be applied.

It cannot be assumed that results obtained from this method and from the normative method are equivalent.

A.2 Terms and definitions

For the purposes of this annex, the following terms and definitions apply.

A.2.1
dissolved adsorbable organically bound halogens after solid phase extraction in waters with high salt content
SPE-AOX
equivalent amount of chlorine, bromine, and iodine contained in organic compounds, expressed as chloride when determined according to this annex

A.3 Interferences

See Clause 4.

A.4 Principle

Filtering of the sample through a filter with an effective pore size of 0,45 µm. Acidification of the filtrate with nitric acid. Adsorption of organic compounds contained in the sample on styrene-divinylbenzene copolymerized resin (first adsorption). Displacement of inorganic halides by rinsing the resin with acidified sodium nitrate solution. Elution of the resin with methanol, dilution of the methanolic solution with water. Treatment of this water/methanol solution as described in Clause 9.

A.5 Reagents

See Clause 6 and the following.

A.5.1 Styrene divinylbenzene copolymerized resin, with narrow grain size distribution, free from halogenated compounds.

Dusty particles may be removed by sieving through a sieve, mesh width < 0,4 mm. Cleaning of the resin may be carried out according to reference [2]. For conditioning, the resin is permanently stored under methanol (A.5.2). See references [3] to [6].

The resin is commercially available and even already filled in suitable adsorption columns[2].

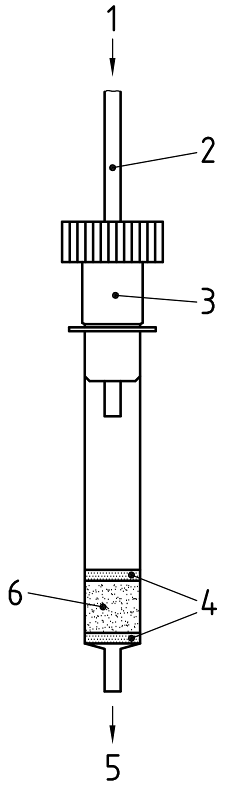
A.5.2 Methanol, CH_4O.

A.6 Apparatus

See Clause 7 and the following.

A.6.1 Adsorption apparatus for the resin, of which an example is given in Figure A.1

Suitable adsorption tube, filled with, for example, 1 ml of styrene divinylbenzene copolymerized resin (A.5.1). Readily filled tubes with for example 1,5 g of adsorption resin are commercially available[2]. The sample is added to the column from above and transported through the resin, for example by applying a piston pump with polytetrafluoroethene (PTFE) tube.



Key

1 sample inlet
2 PTFE stopper
3 PTFE connection tube
4 PTFE frits
5 sample outlet
6 adsorber resin

NOTE Figure taken from reference [2].

Figure A.1 — Example of a resin adsorption apparatus for the SPE-AOX determination

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[2] A suitable product available commercially can be obtained from Normenausschuss Wasserwesen (NAW) im DIN Deutsches Institut für Normung e. V., 10772 Berlin. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

A.7 Sampling and sample pre-treatment

See Clause 8.

A.8 Procedure

A.8.1 Preparation of the test sample

Filter samples containing particles through a filtration apparatus (7.1.1.1) with a pore width of 0,45 µm.

When it is necessary to dilute [with water (6.1) or dilute HNO_3 (6.3.2)], do not use less than 10 ml of the original sample or the filtrate, respectively.

Note the dilution factor. If the dilution factor is greater than 10, dilute in at least 2 steps.

Withdraw a homogeneous sample aliquot of 100 ml.

The SPE-AOX value of the test sample used for analysis should lie within the optimal working range of the apparatus, this is usually between 10 µg/l and 300 µg/l. The chloride concentration of the test sample shall not exceed 100 g/l and the DOC shall be below 1 000 mg/l.

A.8.2 Adsorption on styrene divinylbenzene copolymerized resin

Bring 100 ml of the test sample (A.8.1) to $pH < 2$ with concentrated or dilute HNO_3 (6.3.1 or 6.3.2) and pass it through the column, filled with conditioned resin, by applying a pressure and a flow rate of 3 ml/min. Make sure that the column does not run dry.

Rinse the resin with 50 ml of the nitrate washing solution (6.8) at a flow rate of 3 ml/min.

Discard the sample solution and the washing solution.

Add 1 ml of methanol (A.5.2) to the column and afterwards another 4 ml of methanol. Rinse with water (6.1).

Collect the methanol/water-mixture in a 100 ml measuring flask and add water (6.1) to 100 ml. Treat the obtained test sample in the same way as described in Clause 9, then proceed from A.8.3 to A.10.

For conditioning of the sample and as pretreatment for the next adsorption, repeat the elution step with 5 ml of methanol (A.5.2) and 10 ml of water (6.1) and discard the eluate.

Condition columns that are used for the first time using methanol (A.5.2).

A.8.3 Adsorption on activated carbon

See 9.3.

A.8.4 Combustion and determination of the halide ions

See 9.6.

A.8.5 Blank determination

See 9.4.

A.8.6 Preliminary checks and check tests

See 9.5.

A.8.7 Checking of the completeness of the total adsorption

See 10.2.

A.9 Calculation

See 10.1.

The calculated values for the dissolved adsorbable organically bound halogens after solid phase extraction are designated ρ_{Cl}(SPE-AOX).

A.10 Precision

Tables A.1 and A.2 give the results obtained from an interlaboratory test carried out by DIN in 1999.

Table A.1 — Statistical data for the determination of SPE-AOX using the column procedure (9.3.4)

Sample No	Matrix	l	n	o %	X µg/l	s_r µg/l	CV_r %	s_R µg/l	CV_R %
1	Industrial water	18	69	1,4	83,9	11,7	14,0	19,5	23,3
2	Industrial water	14	55	6,8	321	33,8	10,6	64,1	20,0
3	Industrial water	15	59	11,9	95,8	11,5	12,0	15,5	16,2
4	Leachate	16	61	9,0	108	8,4	7,8	40,7	37,6
5	Sea water	16	62	13,9	72,8	11,6	15,9	16,5	22,7
6	Technical HCl	16	62	12,7	54,5	5,9	10,8	9,8	17,9
7	Blank	12	66	10,8	5,2	1,0	19,3	3,9	74,2

Samples

Sample 1: Industrial waste water (chemical industry), without any alteration
Sample 2: Industrial waste water (chemical industry), SPE-AOX and DOC unchanged, spiked with NaCl
Sample 3: Industrial waste water, AOX and DOC unchanged, spiked with NaCl
Sample 4: Leachate, diluted and subsequently spiked with NaCl
Sample 5: Seawater sample (North Sea), unchanged
Sample 6: Technical HCl as waste in wastes of chemical production

Explanation of symbols

l	is the number of participating laboratories
n	is the number of valid measured values
o	is the number of all outliers
X	the overall means of the ρ_{Cl}(SPE-AOX) values (of the test sample or the blanks respectively), free from outliers
s_r	is the standard deviation of the repeatability (means of the intralaboratory repeatabilities
CV_r	is the coefficient of variation of the repeatability (means of the intralaboratory repeatabilities)
s_R	is the standard deviation of the reproducibility
CV_R	is the coefficient of variation of the reproducibility

Table A.2 — Statistical data for the determination of SPE-AOX applying a combined evaluation of the results of the batch procedure and the stirring procedure (9.3.2 and 9.3.3)

Sample No	Matrix	l	n	o %	X µg/l	s_r µg/l	CV_r %	s_R µg/l	CV_R %
1	Industrial water	17	63	4,6	64,7	7,66	11,8	17,8	27,6
2	Industrial water	15	57	1,7	286	18,1	6,3	44,8	15,7
3	Industrial water	17	64	0	88,2	16,4	18,6	30,1	34,1
4	Leachate	16	62	6,1	104	15,1	14,5	32,9	31,7
5	Sea water	14	53	8,6	62,8	9,08	14,5	12,4	19,7
6	Technical HCl	17	65	0	47,6	7,19	15,1	15,3	32,2
7	Blank	10	63	11,3	7,13	1,08	15,2	4,95	69,5
The explanation of the symbols and the origin of the samples is given in Table A.1									

A.11 Test report

See Clause 12.

Annex B
(informative)

Handling of activated carbon

A possible treatment of activated carbon is described in this annex. If this treatment is chosen, proceed as follows.

a) Activated carbon of appropriate adsorption capacity and low content of inorganic chloride, which is suitable for AOX, is commercially available.

b) The activated carbon may be loaded with adsorbable compounds (including other halogenated compounds) derived from the air. After the opening of a package, the activated carbon will be inactive within 5 d. In order to minimize the blank of the activated carbon, small aliquots of 1,5 g to 2,0 g (daily necessary amounts) are withdrawn and stored in melted off ampoules. The contents of the ampoules shall be used the day of opening of the ampoule. Discard the remainder.

c) Keep the stored remainder sealed. In the case of high blanks in one batch, use another batch after checking the blank.

Annex C
(informative)

Statistical performance characteristics

Tables C.1 to C.3 give the results of an interlaboratory test with 96 participants carried out by CEN in October 1992.

Table C.1 — Results of the shaking procedure specified in 9.3.2

Sample No	Matrix	l	n	o %	X µg/l	x_{true} µg/l	η %	s_{r} µg/l	CV_{r} %	s_{R} µg/l	CV_{R} %
1	River water	56	204	7,3	48,35	45,00	107	3,966 3	8,20	7,503 2	15,5
2	Spiked river water	56	193	13	64,55	45,00	143	6,940 8	10,8	20,689	32,1
3	Synthetic standard	56	214	3,6	90,49	100,0	90,5	4,585 7	5,7	11,741	13,0
4	Spiked synthetic standard	56	218	2,2	131,6	100,0	132	11,744	8,93	37,021	28,1
5	Industrial waste water	56	207	6,8	183,6	195,0	94,1	8,073 7	4,40	18,033	9,82
6	Spiked industrial waste water	56	217	2,3	175,6	195,0	90,1	11,681	6,65	35,859	20,4
7	Spiked industrial waste water	56	207	7,2	199,7	195,0	102	10,567	5,28	24,758	12,4
8	Blank	56	477	9,5	8,04			2,065 9	25,7	5,533 0	68,9

Samples

1 Rhine river water, ρ_{Cl}(AOX): 45 µg/l, chloride: 81 mg/l, DOC: 6 mg/l

2 Rhine river water (same as Sample 1) spiked with NaCl to a content of 1,14 g/l chloride

3 Synthetic solution of *p*-chlorophenol in water solution, theoretical ρ_{Cl}(AOX): 100 µg/l

4 Synthetic solution of *p*-chlorophenol in water solution (same as Sample 4) spiked with NaCl to a content of 975 mg/l chloride

5 Diluted industrial wastewater, ρ_{Cl}(AOX): 195 µg/l, chloride: 160 mg/l, DOC: 10 mg/l

6 Diluted industrial wastewater (same as Sample 5) spiked with potassium hydrogenphthalate to a content of 50 mg/l DOC

7 Diluted industrial wastewater (same as Sample 5) spiked with NaCl to a concentration of 1,04 g/l

8 Deionized water used by the participating laboratories

Explanation of symbols

l is the number of participating laboratories

n is the number of valid ρ_{Cl}(AOX) values; in the case of the blank values, at least four blank values per laboratory were reported

o is the percentage of all outliers

X is the overall mean of the ρ_{Cl}(AOX) values

x_{true} is the conventionally true ρ_{Cl}(AOX) values

η is the recovery

s_{r} is the standard deviation of the repeatability

CV_{r} is the coefficient of variation of the repeatability

s_{R} is the standard deviation of the reproducibility

CV_{R} is the coefficient of variation of the reproducibility

Table C.2 — Results of the column method specified in 9.3.4

Sample No	Matrix	l	n	o	X	x_{true}	η	s_{r}	CV_{r}	s_{R}	CV_{R}
				%	µg/l	µg/l	%	µg/l	%	µg/l	%
1	River water	40	153	3,2	44,58	45,00	99,1	4,024 8	9,03	6,526 3	14,6
2	Spiked river water	40	139	12	57,18	45,00	127	4,695 6	8,22	11,836	20,7
3	Synthetic standard	40	158	0	93,85	100,0	93,8	4,323 8	4,60	8,101 2	8,63
4	Spiked synthetic standard	39	153	0,7	113,4	100,0	113	8,445 8	7,47	17,254	15,2
5	Industrial waste water	40	158	0	193,3	195,0	99,1	10,541	5,46	25,288	13,1
6	Spiked industrial waste water	40	149	2,0	193,7	195,0	99,3	12,235	6,31	28,870	14,9
7	Spiked industrial waste water	39	142	7,8	199,8	195,0	103	10,579	5,29	25,527	12,8
8	Blank	40	354	5,4	8,72			3,381 5	38,8	7,741 0	88,8

The explanation of symbols and origin of the test samples is given in Table C.1.

Table C.3 — Total results (combined evaluation of the results of the column method and the shaking procedure)

Sample No	Matrix	l	n	o	X	x_{true}	η	s_{r}	CV_{r}	s_{R}	CV_{R}
				%	µg/l	µg/l	%	µg/l	%	µg/l	%
1	River water	96	358	5,3	46,77	45,00	104	4,009 4	8,57	7,360 5	15,7
2	Spiked river water	96	339	11	62,42	45,00	139	6,636 6	10,6	18,941	30,3
3	Synthetic standard	96	372	2,1	91,92	100,0	91,9	4,476 4	4,87	10,473	11,4
4	Spiked synthetic standard	95	335	11	117,3	100,0	117	8,762 3	7,49	18,765	16,0
5	Industrial waste water	96	365	3,9	187,8	195,0	96,3	9,221 5	4,91	20,981	11,7
6	Spiked industrial waste water	96	366	2,1	183,0	195,0	93,8	11,908	6,51	34,323	18,8
7	Spiked industrial waste water	95	349	7,4	199,8	195,0	102	10,572	5,29	25,038	12,5
8	Blank	96	831	7,8	8,33			2,706 1	32,5	6,569 3	78,9

The explanation of symbols and origin of the test samples is given in Table C.1.

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ICS 13.060.50

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