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Water quality — Determination of adsorbable organic halogens (AOX)

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

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9562 was prepared by Technical Committee ISO/TC 147, *Water quality*.

Annexes A and B form an integral part of this International Standard. Annex C is for information only.

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Introduction

AOX is a parameter used for control purposes in water. It covers the total amount of organically bound chlorine and bromine which can be adsorbed on activated carbon. The method includes the following pretreatment and adsorption steps :

- a) stripping of the volatile organic halogens (see 8.1.1);
- b) adsorption of the organic halogens either by shaking (see 8.1.2.1) or by column adsorption (see 8.1.2.2).

Although investigations have shown that the recoveries for almost all tested substances are almost quantitative, there are some exceptions, for example hydrophilic substances like monochloroacetic acid or trichlorotrifluoroethane.

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Water quality — Determination of adsorbable organic halogens (AOX)

1 Scope

1.1 This International standard is intended for the direct determination of the organic halogenated compounds including volatile compounds (see 8.1.1) adsorbable on activated carbon (AOX), in waters with an AOX value above 10 µg/l of the organically bound halogens chlorine, bromine, and partially iodine (see 1.4) (determined as the chloride). The content of dissolved organic carbon (DOC) must be less than 10 mg/l and the concentration of inorganic chloride less than 1 g/l. Samples with higher concentrations must be diluted prior to analysis (see annex A). If the concentration of organic halogens in the sample is below 10 µg/l and the DOC value is correspondingly low, a larger sample volume than that given in the instructions may be selected. In the case of samples which contain suspended matter, the halogen compounds present in the latter are also covered by the determination.

1.2 Interferences with filtration, caused by colloids during the separation of the activated carbon from the aqueous phase, can be avoided, for example, by the addition of filtering aids such as diatomaceous earth or overcome by flocculating the loaded carbon.

1.3 In the presence of active chlorine, high results in the AOX determination may be caused. A reaction of these oxidizing agents with organic constituents of the sample and with the activated carbon can be prevented by the addition of reducing agents, for example sodium sulfite, immediately after sampling.

1.4 Inorganic iodine compounds interfere in the adsorption and detection. Organic iodine compounds may lead to non-reproducibly high results.

1.5 Larger concentrations of inorganic bromide may interfere.

1.6 Low soluble inorganic halides can cause high results. Living cells (for example micro-organisms, algae) can lead to high results due to their chloride content. In this case, the sample shall not be analysed until at least 8 h after acidification.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International

Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1 : 1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2 : 1982, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3 : 1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 8245 : 1987, *Water quality — Guidelines for the determination of total organic carbon (TOC).*

3 Definitions

For the purposes of this International Standard, the following definitions apply:

3.1 adsorbable organic halogens (AOX): The amount of the halogens chlorine and bromine contained in organic compounds, determined as chloride according to this standard procedure.

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. Stripping of the water sample (if appropriate) and combustion of volatile organic halogens in a separate step. Adsorption on activated carbon of the organic substance in the water sample. Displacement of the inorganic halogen by rinsing with sodium nitrate solution. Combustion of the loaded carbon in an oxygen stream. Absorption of the hydrogen halides and determination of their mass concentration, for example by microcoulometry.

5 Reagents

Use only reagents of recognized analytical grade. Test the water, the chemicals and the gases used for their purity. Ensure that the AOX content is negligibly small compared with the lowest AOX content which is to be determined. Store the purified water in a glass bottle over activated carbon (5.1).

5.1 Activated carbon

For handling and pretreatment of the activated carbon see annex B.

The adsorption capacity of the activated annex B carbon to be used is indicated by the iodine number (see annex B). The blank reading of the rinsed activated carbon should be less than 15 µg of chloride per gram of activated carbon.

NOTE — For the procedure described in 8.1.2.1, powdered activated carbon with a grain size of about 50 µm is suitable. For the procedure described in 8.1.2.2, activated carbon with a grain size of 100 µm and a narrow grain size distribution is to be preferred.

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

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

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

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

5.6 Nitrate, stock solution.

Dissolve 17 g of sodium nitrate (NaNO_3) in water in a 1 000 ml one-mark volumetric flask, add 1,4 ml of nitric acid (5.2) and make up to the mark with water.

5.7 Nitrate, wash solution.

Dilute 50 ml of the nitrate stock solution (5.6) in a 1 000 ml one-mark volumetric flask and make up to the mark with water.

5.8 Sodium sulfate, solution, $c(\text{Na}_2\text{SO}_3) = 0,2$ mol/l.

5.9 *p*-Chlorophenol, stock solution corresponding to 1 mg of organic chlorine per litre.

Dissolve 72,5 mg of *p*-chlorophenol ($\text{C}_6\text{H}_5\text{ClO}$) in 100 ml of water. Pipette 5 ml of this solution into a 1 000 ml one-mark volumetric flask, and make up to the mark with water.

1 ml of this standard solution contains 1 mg of organic chlorine.

5.10 *p*-Chlorophenol, standard solutions.

Pipette 1 ml, 5 ml, 10 ml, 20 ml and 25 ml of the stock solution (5.9) into 100 ml one-mark volumetric flasks and make up to the mark with water.

The solutions must be prepared daily.

6 Apparatus

Usual laboratory apparatus and

6.1 Apparatus for stripping, combustion and detection.

6.1.1 Combustion apparatus, for example consisting of a furnace, capable of heating to at least 950 °C, equipped with a quartz tube, 2 cm to 3 cm in diameter and 30 cm long (an example is given in figure C.1).

6.1.2 Quartz boat, to fit in the tube (see 6.1.1).

6.1.3 Microcoulometer, capable of determining 1 µg of chlorine with a standard deviation of less than 10 %, or an equivalent device to detect the chloride ions.

6.1.4 Absorber, filled with sulfuric acid, to dry the gas stream. Make sure that no backflush can occur.

6.1.5 Gas inlet, made from glass, metal or polytetrafluoroethylene (PTFE), for the stripping procedure.

6.2 Apparatus for adsorption, according to 8.1.2.1.

6.2.1 Filtration apparatus, for example with a filter funnel, capacity $V = 0,15$ litre, filter diameter 25 mm.

6.2.2 Polycarbonate membrane filter, with low chloride content, 25 mm in diameter and 0,4 µm in pore diameter.

6.2.3 Conical flask, with conical socket.

6.2.4 Mechanical shaker, for example with a carrier plate.

6.3 Adsorption apparatus, according to 8.1.2.2.

6.3.1 Adsorption unit, for example a unit consisting of a piston pump with PTFE hose and adsorption tubes, 2 mm to 3 mm in internal diameter and 40 mm to 50 mm long, packed with approximately 50 mg of activated carbon between ceramic wool.

7 Sampling and sample pretreatment

Use only glass vessels for sampling, transport and storage.

7.1 Immediately add up to 5 ml of sodium sulfite solution (5.8) per 100 ml of sample to samples which contain oxidizing agents (see clause 1).

7.2 Adjust the sample to a pH value between 1,5 and 2,0 with nitric acid (5.2), and let it stand for 8 h if necessary (see clause 1).

7.3 Fill the glass vessels to the brim without any bubbles.

7.4 Analyse the water sample as quickly as possible after sampling. If storage is unavoidable, store the acidified sample at 4 °C but for not longer than 3 days.

7.5 Bring the water sample to room temperature prior to analysis.

8 Procedure

8.1 Separation steps

8.1.1 Stripping and determination of volatile halogenated compounds.

This stripping procedure can be omitted if the sample contains less than 50 % of volatile halogenated compounds.

Place a sample of, for example, 100 ml, in a gas-wash bottle.

Immerse a wash bottle insert (6.1.5) with hose connections to an oxygen supply on one side and to a combustion tube (see 6.1.1) on the other side, as deeply as possible into the sample.

Regulate the oxygen flow to 150 ml/min; ensure uniform distribution of the bubbles.

Feed the gas mixture into the combustion apparatus (6.1.1) at about 950 °C.

Purge for at least 10 min or until the reaction is finished (no raising signal in the voltmeter).

Determine the resulting halides coulometrically as specified in clause 10.

8.1.2 Adsorption steps

The adsorption may be carried out using the procedure given in either 8.1.2.1 or 8.1.2.2.

8.1.2.1 Adsorption by shaking

Take the sample, if necessary pretreated as in 8.1.1 and place it on a mechanical shaker (6.2.4).

If the wash bottle cannot be fixed on a mechanical shaker, transfer to a conical flask (6.2.3) and rinse the wash bottle with a small amount of water (clause 5).

If purging is not carried out, place 100 ml of the appropriately prepared water sample in a conical flask of, for example, 250 ml nominal capacity.

Add 5 ml of nitrate stock solution (5.6) to the solution and check that the pH value is less than 2.

Add 50 mg of activated carbon (5.1) and shake the suspension for at least 1 h.

Filter the suspension through a polycarbonate membrane filter (6.2.2). If necessary, filter by suction.

Wash the filter cake with about 25 ml of nitrate wash solution (5.7) in several portions. After filtration, place the moist filter cake together with the polycarbonate filter into a quartz combustion boat and continue as described in 8.2.

NOTES

1 Completeness of the adsorption is indicated by a constant DOC value and can be checked by DOC measurements.

2 Different sample volumes (for example 50 ml and 100 ml) may be used to check the completeness of adsorption. In this case the difference in AOX value should be less than 10 %. In the case of effluents with high-molecular constituents (for example pulp mill effluents), longer adsorption times than 1 h may be necessary. In this case, the shaking period shall be extended, for example overnight.

3 The filter cake shall not be sucked to dryness, in order to avoid high results (contamination by laboratory air).

4 If there are difficulties in filtration, the solids can be flocculated. Add 0,5 ml of an aqueous aluminium sulfate solution (6,3 g/l) to the activated carbon suspension, with stirring. Adjust the pH value of the suspension to between 6,8 and 7,2 by means of solid sodium carbonate. Add whilst stirring, 0,2 ml to 0,4 ml of an aqueous solution of a partially hydrolyzed polyacrylamide (0,2 g/l). Continue to stir for a short period and then let the resulting flocs settle. Decant the supernatant liquid and subject the flocs to further treatment as described in the fifth paragraph of 8.1.2.1.

8.1.2.2 Adsorption on activated carbon in columns

If the sample was pretreated according to 8.1.1, add 5 ml of nitrate stock solution (5.6) to the sample.

If pretreatment according to 8.1.1 was omitted, add 5 ml of nitrate stock solution to a sample volume of, for example, 100 ml of the water pretreated as described in clause 7 and check that the pH is less than 2.

Pass the sample through the adsorption unit (6.3.1) arranged in series and charged with activated carbon at a flow rate of 3 ml/min.

Wash each column with 10 ml to 20 ml of nitrate wash solution (5.7) at a flow rate of 3 ml/min.

Transfer the moist activated carbon and the ceramic wool from each column separately into quartz combustion boats and ignite them individually, as described in 8.2.

NOTE — The AOX value obtained from the second adsorption column should not exceed 10 % of the AOX value from the first column. Otherwise, the sample shall be diluted (see annex A).

8.2 Combustion

The manufacturer's instructions shall be followed.

The temperature in the combustion chamber (6.1.1) shall be at least 950 °C, and the other operating parameters are selected in accordance with those given by the manufacturer of the apparatus.

8.2.1 Connect the oxygen supply with the combustion tube and the tube with the absorber (see figure C.1).

NOTE — Back-siphoning of the sulfuric acid into the combustion tube, caused by a fall in temperature or pressure, must be avoided.

8.2.2 Adjust the oxygen flow rate to about 150 ml/min.

8.2.3 Slowly introduce the quartz boat into the heated zone of the tube, in order to ensure that the moisture can escape slowly from the sample.

NOTE — The furnace dimensions, the residence time, the temperature and the gas flow may affect the result.

8.3 Calibration and verification

The microcoulometer should be checked daily in the appropriate range.

8.3.1 Checking of the microcoulometer

Inject 1 µl, 2 µl, 3 µl, 4 µl, 5 µl, 6 µl, 7 µl, 8 µl, 9 µl and 10 µl of the hydrochloric acid solution (5.3) directly into the titration cell.

Measure the quantity of charge transferred in each case.

Fit a regression line for the series of measured values thus obtained by means of linear regression, in accordance with equation (1):

$$Q = a \times Q_t + b \quad \dots (1)$$

where

Q is the measured quantity, in coulombs, of charge transferred;

Q_t is the theoretical quantity, in coulombs, of the charge;

a is the slope of the regression line (current yield of the electrolysis);

b is the ordinate intercept of the regression line, in coulombs.

The theoretical quantity of charge is obtained from equation (2);

$$Q_t = V \times c_{Cl} \times F \quad \dots (2)$$

where

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

c_{Cl} is the actual concentration, in moles of Cl^- per litre, of the hydrochloric acid solution;

F is the Faraday constant: $F = 96\,487\text{ C/mol}$.

8.3.2 Verification of the entire procedure

Analyse five standard solutions (5.10) and an additional blank of known mass concentration of AOX. Follow the procedure as described in 8.1.2.1 or 8.1.2.2.

NOTE — The result of the verification is acceptable if the correlation coefficient is greater than 0,999. If not, the data points should be evaluated graphically. The diagram will show outliers, high variances, or non-linearity, which may be the reasons for the non-satisfying results. For a daily check of the overall procedure, measure one point in the central part of the working range. The difference between the measured value and the theoretical value shall not exceed 10 % (recovery rate 91 % to 110 %).

8.4 Blank determination

8.4.1 General

The total blank shall not exceed 3 µg or 30 µg/l respectively, otherwise check the adsorption step, the combustion step and the microcoulometric determination separately.

Considerable contamination of the laboratory air with organic halogen compounds can arise from laboratory chemicals or other sources, for example correcting liquid for typing machines. In order to prevent high results, the carbon filter cake shall not be sucked to dryness in any of the determinations. If the laboratory air is highly contaminated, even the dead volume of the purging apparatus can cause high results. If flocculation aids and filtering aids are added, the blank shall be determined correspondingly, taking these materials into account.

8.4.2 Determination of the blank according to 8.1.2.1

Suspend 50 mg of activated carbon (5.1) in about 50 ml of nitrate wash solution (5.7) and shake for 1 h.

Filter off the washed carbon, as described in 8.1.2.1, and determine the content of organically bound chlorine.

8.4.3 Determination of the blank according to 8.1.2.2

Proceed as specified in 8.1.2.2 using 100 ml of water (clause 5) instead of the sample.

9 Expression of results

9.1 Method of calculation

Calculate the mass concentration of adsorbable organic halogens (AOX) from equation (3):

$$\rho_{Cl} = \left(\frac{N_1}{V_1} + \frac{N_2 - N_0}{V_2} \right) \times \frac{M \times a}{F} \quad \dots (3)$$

where

ρ_{Cl} is the mass concentration, in micrograms per litre, of AOX as Cl^- ;

N_0 is the blank, in coulombs, according to 10.3;

N_1 is the measured value of the stripped organic halogens as Q , in coulombs;

N_2 is the measured value of the adsorbed organic halogens, as Q , in coulombs;

M is the molar mass of chloride:

$M = 35,45 \times 10^6 \mu\text{g/mol};$

V_1 is the volume, in litres, of the stripped sample;

V_2 is the volume, in litres, of the sample used for adsorption;

a and F have the same meanings as in equations (1) and (2).

If the sample was not stripped, the expression N_1/V_1 is omitted.

NOTE — The results from the second adsorption column do not enter into the calculation and are only used as a check for the completeness of the adsorption step.

The results shall be expressed in micrograms of chloride per litre or milligrams of chloride per litre to two significant figures.

Table 1 — Precision data

Type of water	l	n	n_a	\bar{x}	σ_r	VC_r	σ_R	VC_R
Drinking water	24	96	4	19,0	2,22	11,7	3,86	20,3
Surface water	26	103	5	69,0	3,02	5,7	8,82	12,8
Effluent	26	104	4	777,0	23,97	3,1	103,46	13,3

where

- l is the number of laboratories;
- n is the number of valid measured values;
- n_a is the number of outliers;
- \bar{x} is the overall mean, in micrograms per litre (after rejection of outliers);
- σ_r is the repeatability standard deviation, in micrograms per litre;
- VC_r is the repeatability variation coefficient, as a percentage;
- σ_R is the reproducibility standard deviation, in micrograms per litre;
- VC_R is the reproducibility variation coefficient, as a percentage.

EXAMPLE

Content of adsorbable organic halogens (AOX), calculated as chloride:

74 $\mu\text{g/l}$

6,2 mg/l

9.2 Precision

An inter-laboratory test carried out in January 1985 yielded the data shown in table 1.

10 Test report

The report shall contain the following information:

- a) a reference to this International Standard;
- b) precise identification of the water sample;
- c) if relevant, a statement that a stripping procedure was carried out;
- d) the adsorption procedure used;
- e) expression of the results as specified in the last paragraph of 9.1;
- f) details of any deviation from the procedure specified in this International Standard or any other circumstances that may have influenced the result.