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ISO 9562

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

Qualité de l'eau — Dosage des halogènes adsorbables organiquement liés (AOX)

Reference number
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Contents

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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 3.

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

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

This second edition cancels and replaces the first edition (ISO 9562:1989), which has been technically revised.

Annexes A and B of this International Standard are for information only.

Introduction

The parameter AOX is an analytical convention 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.

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

1 Scope

This International 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 method is applicable to concentrations of inorganic chloride ions in the test sample (see clause 9) of 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.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

3 Terms and definitions

For the purposes of this International Standard, 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 in accordance with this International Standard

3.2
dissolved organic carbon
DOC
amount of organic carbon present in a water sample after filtration through a membrane filter of pore size 0,45 µm

4 Principle

The water sample is acidified with nitric acid. Organic compounds contained in the sample are adsorbed onto activated carbon, either by a shaking procedure or by column adsorption. Inorganic halides are displaced by rinsing the activated carbon with acidified sodium nitrate solution. Combustion of the loaded carbon is then carried out in an oxygen stream. Adsorption of the hydrogen halides thus formed is followed by determination of the halide ions by an argentometric titration, such as microcoulometry. The result is expressed as the mass concentration of chloride.

5 Interferences

5.1 High AOX values can result from the presence of free 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.

5.2 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.

5.3 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.

5.4 Insoluble inorganic halides can cause positive bias.

5.5 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 analysed until at least 8 h after acidification.

5.6 For samples with high chloride concentrations (approximately 1 g/l) the shaking procedure (see 9.3.1) can result in higher interferences (positive bias, see 10.2) than the column procedure (see 9.3.2).

6 Reagents

Use only reagents of recognized analytical grade and water of grade 1 in accordance with ISO 3696.

The purity of water, reagents and gases shall be confirmed.

For successful application of the method, the AOX content must 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 content in the total blank (see 9.6).

6.1 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 > 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 Nitric acid, HNO_3, $\rho = 1{,}4$ g/ml, 65 % mass fraction solution.

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

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

6.4 Sulfuric acid, H_2SO_4, ρ = 1,84 g/ml.

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

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

Dissolve 17 g of sodium nitrate ($NaNO_3$) in water in a 1 000 ml volumetric flask, add 1,4 ml of nitric acid (see 6.2), and make up to volume with water.

6.7 Nitrate washing solution, $c(\mathrm{NaNO_3})$ = 0,01 mol/l.

Pipette 50 ml of the nitrate stock solution (see 6.6) in a 1 000 ml volumetric flask, and make up to volume with water.

6.8 Sodium sulfite solution, $c(\mathrm{Na_2SO_3})$ = 1 mol/l.

Dissolve 126 g anhydrous Na_2SO_3 in water in a 1 000 ml volumetric flask and make up to volume with water.

6.9 4-Chlorophenol, stock solution, AOX = 200 mg/l.

Dissolve 72,5 mg of 4-chlorophenol (C_6H_4ClOH) in water in a 100 ml volumetric flask and make up to volume with water.

6.10 4-Chlorophenol, working solution, AOX = 1 mg/l.

Pipette 5 ml of 4-chlorophenol, stock solution, (see 6.9) into a 1 000 ml volumetric flask, and make up to volume with water.

6.11 2-Chlorobenzoic acid, stock solution, 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.

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

6.12 2-Chlorobenzoic acid, working solution, AOX = 1 mg/l.

Pipette 4 ml of 2-chlorobenzoic acid, stock solution (see 6.11), into a 1 000 ml volumetric flask, and make up to volume with water.

The stock solutions (see 6.9 and 6.11) may be stored for at least 1 month and the working solutions (see 6.10 and 6.12) for 1 week at 4 °C in glass bottles.

6.13 Standard solutions for checks on the overall procedure (9.5.2)

Pipette 1 ml, 5 ml, 10 ml, 20 ml, and 25 ml of the working solutions (see 6.10 or 6.12) into five separate 100 ml volumetric flasks, and make up to volume with water.

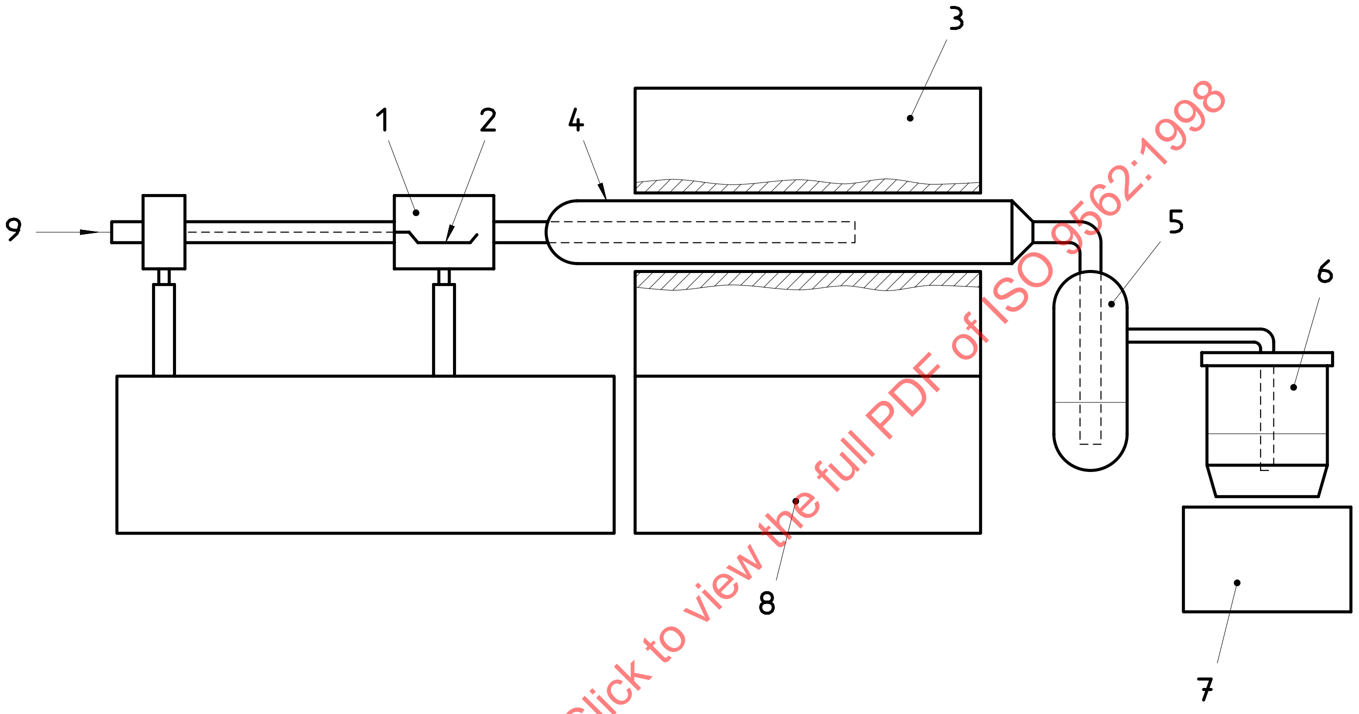
The AOX mass concentration of these solutions is 10 µg/l, 50 µg/l, 100 µg/l, 200 µg/l and 250 µg/l respectively.

The standard solutions shall be prepared daily.

7 Apparatus

7.1 Apparatus for combustion and detection

7.1.1 Combustion apparatus, consisting of 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 example in Figure 1).



Key

1 Sample inlet for AOX	6 Titration cell
2 AOX sample	7 Stirrer
3 Furnace	8 Control device for temperature, gas flow
4 Combustion tube	9 Combustion gas inlet
5 Absorber filled with sulfuric acid	

Figure 1 — Schematic diagram of example of an AOX apparatus

7.1.2 Quartz container, to fit in the quartz tube.

7.1.3 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.

7.1.4 Absorber, filled with sulfuric acid (see 6.4), to dry the gas stream and designed so that the acid does not backflush into the furnace.

7.1.5 Syringe, to pipette volumes of 1 µl to 10 µl of hydrochloric acid (see 6.3).

7.2 Adsorption unit

7.2.1 Adsorption unit for shaking procedure (9.3.1).

7.2.1.1 Filtration apparatus, for example with a funnel capacity of 0,15 l and filter diameter of 25 mm.

7.2.1.2 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.

7.2.1.3 Conical flask (Erlenmeyer flask).

7.2.1.4 Mechanical shaker for the flasks described in 7.2.1.3, equipped for example with a carrier plate.

7.2.2 Adsorption unit for column adsorption (9.3.2).

A suitable pump, for example a piston pump, with polytetrafluoroethene (PTFE) hose 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 prefilter, packed for example with ceramic wool (7.2.3) as filtration material, connected to the inlet, is necessary.

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

8 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 to contain oxidizing agents, immediately add at the time of sampling up to 10 ml of sodium sulfite solution (6.8) per litre of sample.

To test samples for the presence of free chlorine before or after the addition of sodium sulfite (see 6.8), 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 6.2) per litre of sample and completely fill the sample bottle leaving no air gap; if necessary (see 5.5), 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.

Analyse the water sample as soon as possible after sampling or, in the presence of living cells (see 5.5), 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 be started within 24 h after sampling. A maximum storage time is not given, since individual circumstances will dictate the requirements.

9 Procedure

9.1 General

It is absolutely essential that tests conducted in accordance with this International Standard are carried out by suitably qualified staff.

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.

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.

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.

9.3 Adsorption

9.3.1 Shaking procedure

Transfer the test sample (see 9.2) into a stoppered conical flask (see 7.2.1.3), the nominal capacity of which shall not exceed 250 ml in order to restrict the headspace.

Add 5 ml of nitrate stock solution (see 6.6) to the flask and ensure that the pH is less than 2.

Add 50 mg of activated carbon (see 6.1), stopper the flask and shake the suspension for 1 h.

Filter the suspension through a filtration system (see 7.2.1.1). 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 6.7), applying the solution in several portions. It is essential that the filter cake is not sucked to dryness, since this may lead to positive bias, caused for example by contaminated laboratory air.

Place the moist filter and the filter cake into the quartz combustion container (see 7.1.2) and proceed in accordance with 9.4.

To check the completeness of the adsorption, use:

a) either two separate test sample aliquots and/or dilution steps, or

b) add another 50 mg of activated carbon after completion of the first adsorption step.

NOTE 1 In case a), the AOX values of both measurements should not deviate from each other by more than 10 %. In case b), 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 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 9), it is recommended to use the column procedure (see 9.3.2).

9.3.2 Column procedure

Add 5 ml of nitrate solution (see 6.6) to the test sample (see 9.2).

Ensure that the pH is below 2, if not, add more nitric acid (see 6.2).

Pass the sample through the adsorption columns arranged in series (see 7.2.2) at a flowrate of 3 ml/min.

Wash the columns with approximately 25 ml of the nitrate washing solution (see 6.7), at a flowrate 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 prefilter, if used (see 7.2.2) as described in 9.4.

Use the AOX results of both columns to check the completeness of the adsorption.

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 that the determination 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 6.7) 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.

9.4 Combustion

The temperature in the combustion chamber (see 7.1.1) 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 7.1.4).

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 flowrate (see 6.5) to approximately 150 ml/min.

Introduce the quartz container (see 7.1.2) 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 9.2), the dimensions of the furnace, residence time, combustion temperature, and the adjustment of the gas flowrate (see 6.5 and 9.4) will depend on the type of apparatus and may also affect the result.

9.5 Operational tests of the method

9.5.1 Checks on the instrumentation used to determine halide concentration

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

a) Inject directly with a syringe (see 7.1.5) a volume within the range of 5 µl to 8 µl of the hydrochloric acid solution (see 6.3) into the titration cell.

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

Coulometry theory assumes a 100 % current yield. But for practical purposes, it is important to determine the actual current yield. Obtain the correction factor, a, by using equation (1):

$$Q = a \cdot Q_t \tag{1}$$

where

Q is the measured quantity of charge for the hydrochloric acid sample, in coulombs;

Q_t is the theoretical quantity of charge for the hydrochloric acid sample, in coulombs;

a is the correction factor.

Obtain the theoretical quantity of charge, Q_t, by using equation (2):

$$Q_t = V \cdot c_{Cl} \cdot F \tag{2}$$

where

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

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

F is the Faraday constant, and has a value of 96 487 C/mol.

9.5.2 Checks on the overall procedure

9.5.2.1 Daily procedure

Check the entire procedure daily by running a standard solution (see 6.13) with a concentration in the middle of the working range of the instrument.

The value so obtained and the theoretical value shall not deviate by more than 10 %.

9.5.2.2 Initial check

Carry out an initial check as follows when this standard method is introduced into the laboratory, if essential parts of the apparatus are changed, if on the daily check (see 9.5.2.1) a deviation of > 10 % is obtained or if different or new staff are employed to carry out the determinations.

Analyse a blank sample and at least five standard solutions (see 6.13) and compare the measured results with the nominal values.

Test the correlation of the measured AOX values with the nominal AOX values.

NOTE The result of this test is acceptable if the coefficient of correlation is ⩾ 0,999 and the slope of the calibration function is within the range 0,95 to 1,05. In addition, the data can be evaluated graphically which will identify any outliers present. High variances or nonlinearity may cause unsatisfactory results.

9.6 Blank determination

9.6.1 General

The measured value for the total blank shall not exceed 3 µg (equivalent to 30 µg/l on a test sample volume of 100 ml), otherwise the adsorption step, the combustion step, and the argentometric titration shall be checked separately. If the blank value exceeds 10 µg/l, use the standard deviation of the blank value to determine the detection limit.

Considerable contamination of the laboratory air can arise from laboratory chemicals or other sources (for example correction liquid used for typewriting).

9.6.2 Procedure for the determination of the blank

Use 100 ml of acidified water in place of the sample and analyse in the same way as described for the analytical sample (see 9.4).

NOTE If the test sample (see 9.2) contains, as well as a low AOX concentration, a chloride concentration of approximately 1 g/l, a significant positive bias can be obtained. In these cases it is recommended that instead of acidified water, 100 ml of acidified chloride solution (with the same chloride concentration as in the test sample, acidified with HNO_3 to pH < 2) is used. By this means any bias $\leqslant$ 5 %, caused by inorganic chloride, can be compensated for.

10 Expression of results

10.1 Method of calculation

Calculate the mass concentration of adsorbable organically bound halogens, expressed as chloride Q_{Cl} (AOX) using equation (3):

$$Q_{\mathrm{Cl}}\,(\mathrm{AOX}) = \frac{N - N_0}{V} \cdot \frac{M \cdot a}{F} \cdot D$$

where

N_0	is the blank, in accordance with 9.6, in coulombs;
N	is the measured value of the adsorbed organically bound halogens, as Q, in coulombs;
M	is the molar mass of chloride ($M = 35{,}45 \times 10^6$ µg/mol, if the result is expressed in micrograms per litre, and $M = 35{,}45 \times 10^3$ if the result is expressed in milligrams per litre);
V	is the volume of the sample for the adsorption, in litres;
F, a	are as defined in equations (1) and (2);
D	is the dilution factor, if applicable.

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

EXAMPLES:

74 µg/l

6,2 mg/l

10.2 Performance characteristics

Annex B provides the results of an interlaboratory test carried out in October 1992.

11 Test report

The test report shall contain at least the following information:

a) reference to this International Standard;

b) precise identification of the water sample;

c) adsorption, combustion, and determination methods used;

d) expression of results, in accordance with 10.1;

e) any factors which may have influenced the result.

Annex A
(informative)

Storage of activated carbon

Activated carbon of an adequate adsorption capacity and of low content of inorganic chloride, suitable for the AOX determination, is commercially available. Activated carbon can be contaminated with adsorbable compounds (including other organic halogens) from the air, and can thus become inactive within 5 days after opening the package.

In order to keep the carbon blank low, small quantities of 1,5 g to 2 g (daily quantity) are taken and kept in a sealed glass ampoule.

The contents of the ampoule should be used on the day of its opening. The unused remainder is discarded at the end of the day.

The remaining stock remains sealed. If the carbon blank is too high, another batch should be used, after checking its blank.