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Soil, sludge and treated biowaste Solid materials — Determination of adsorbable organically bound halogens (AOX)

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Foreword

This document (TC BT WI) has been prepared by Technical Committee CEN/TC BT “Horizontal”, the secretariat of which is held by DS .

The standard is applicable and validated for several types of matrices. The table below indicates which ones.

Material	Validated	Document
Soil	<input checked="" type="checkbox"/>	[reference]
Sludge	<input checked="" type="checkbox"/>	[reference]
Biowaste	<input checked="" type="checkbox"/>	[reference]

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Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study "Horizontal European standard for determination of AOX in sewage sludge and comparable matrices" in the project and aims at evaluation of the latest developments in assessing AOX in sludge, soil, treated biowaste and neighbouring fields. After an evaluation study, in which e.g. the ruggedness of the method was studied, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis a horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole "chain of measurement" (from sampling to analyses). **A beneficial feature of this approach is that "modules" can be replaced by better ones without jeopardizing the standard "chain".**

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

1 Scope

This European Standard describes an empirical method for the direct determination of organically bound chlorine, bromine and iodine (but not fluorine) adsorbed and occluded to the sample matrix. Non-volatile organically bound halogens adsorbable on activated carbon present in the aqueous phase of the sample prior to drying or adsorbed to sample surface are included in the determination.

This European Standard is intended for analysis of solid material, for example sludge or soil in concentrations ranging from 5 mg/kg dry matter to approximately 6 g/kg dry matter. The exact concentration range covered depends on the instrument used.

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.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods*.

CSS99031 *Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan*

CSS99058 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions*

CSS99057 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques*

CSS99032 *Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field*

CSS99059 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery*

CSS99060 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan*

CSS99034 *Soil, sludge and treated biowaste – Pre-treatment for organic and inorganic characterisation*

CSS99022 *Soil, sludge and treated biowaste – Determination of dry matter – Gravimetric method*

3 Definitions

For the purpose of this European Standard, the following definition applies :

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 European Standard.

4 Principle

Activated carbon is added to dried, homogenised solid sample. Inorganic halides are eluted and at the same

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time water soluble organic compounds are adsorbed onto the activated carbon by shaking with acidified nitrate solution.

The loaded carbon / sample mixture is combusted in an oxygen stream.

The hydrogen halides produced are absorbed 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

Sparingly soluble or occluded inorganic halides are included in the determination and may, if present, give a significant positive bias. Adequate washing is essential to remove inorganic interference.

Organic bromine and iodine compounds may, during combustion, lead to the formation of elemental bromine or iodine respectively or to the formation of halogen oxides. These fractions of AOX may be incompletely determined, thus leading to negative bias.

Halogenated substances that volatilise during the drying step at 105 °C are lost.

6 Reagents

6.1 General

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

The AOX contribution from water, reagents and gases should be significantly less than the lowest AOX content to be determined. The overall AOX content of water, chemicals, and gases shall be checked by measuring the total blank (see 9.6).

6.2 Activated carbon

Use an activated carbon of about 10 µm to 50 µm grain size.

For the storage of activated carbon, see annex A.

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

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

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

The molarity shall precisely be known, since the acid is used for checking the microtitration (see 9.4.3).

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

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

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

Dissolve 17 g of sodium nitrate (NaNO_3) in water in a 1 000 ml volumetric flask, add 15 ml of nitric acid (6.3), and make up to volume with water.

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

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

6.9 Methanol, CH₃OH.

6.10 4-Chlorophenol stock solution, Equivalent to AOX = 2,0 g/l

Dissolve 0,725 g of 4-chlorophenol (C₆H₅ClO) in methanol (6.9) in a 100 ml calibrated flask and make up to volume with methanol (6.9).

6.11 4-Chlorophenol working solutions, Equivalent to AOX = 0,1 g/l and 0,5 g/l AOX, respectively

Pipette 5 ml and 25 ml of 4-chlorophenol, stock solution (6.10) into two separate 100 ml calibrated flasks, and make up to volume with methanol (6.9).

The stock solution (6.10) may be stored for at least one month and the working solutions (6.11) for one week in a refrigerator in glass bottles.

7 Apparatus

7.1 Apparatus for combustion and detection

NOTE 1 Suitable commercial equipment is available for combustion and detection. This comprises of the following units.

7.1.1 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 annex B).

NOTE 2 It is essential that the combustion temperature is sufficient. Temperatures lower than specified above give low recovery of AOX and increased variability.

7.1.2 Quartz sample boat, 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 (6.5), 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 (6.4) or 4-chlorophenol solutions (6.10 and 6.11).

7.2 Equipment for adsorption

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

7.2.2 Low-halide polycarbonate membrane filter, to fit the filtration apparatus (7.2.1), with a pore size of 0,45 µm, or any equivalent filtration material, such as a dedicated quartz filter for AOX determination.

7.2.3 Conical flask (Erlenmeyer flask) of 25 ml capacity with ground glass stopper or 12 ml to 20 ml screw cap vial with PTFE lined cap.

7.2.4 Mechanical shaker for the flasks described in 7.2.3 above, equipped for example with a carrier plate.

7.3 Equipment for sample preparation

7.3.1 Porcelain evaporating dish

7.3.2 **Oven** with forced ventilation or natural ventilation through adjustable vents adjustable to $(105 \pm 5) ^\circ\text{C}$.

7.3.3 **Desiccator** provided with a suitable desiccant.

7.3.4 **Analytical mill** or porcelain mortar.

8 Sampling and sample pre-treatment

8.1 Sampling

Sampling shall be carried out in accordance with sampling standards CSS99031-32 and 99057- 60..

Samples shall be stored in suitable containers with an appropriate closure material such as PTFE. Samples to be frozen may be stored in aluminium containers pre-cleaned by heating to $450 ^\circ\text{C}$ for minimum four hours or by rinsing with a non-chlorinated solvent.

Samples shall be kept cold at a temperature $< 8 ^\circ\text{C}$) and in the dark. The sample pre-treatment should take place within 24 hours of sampling. Alternatively, samples may be frozen ($-18 ^\circ\text{C}$) directly after sampling and kept frozen for a maximum of one month before sample pre-treatment.

8.2 Sample pre-treatment

Transfer a sub-sample, homogenized according to CSS99034.

Dry the sample to constant weight at $(105 \pm 5) ^\circ\text{C}$ as described in CSS99022

Cool the dried sample in a dessicator, comminute and homogenize in an analytical mill or porcelain mortar (7.3.4) to a particle size of no more than 0,1 mm.

Store the ground material in a desiccator or a tightly closed glass container.

NOTE The homogenised wet sample portion of approximately 100 g may alternatively be freeze-dried, which in some cases makes the homogenizing of the dried sample easier.

9 Procedure

9.1 General

The test sample taken for analysis shall have an AOX value within the optimal working range of the instrument, which is generally between $1 \mu\text{g}$ and $20 \mu\text{g}$ to $30 \mu\text{g}$ (absolute amount).

9.2 Adsorption and inorganic halide removal

Ensure that the dried, ground sample is homogenised by stirring or shaking before taking the sub-sample. Prepare the sample for combustion as follows:

- a) Transfer a homogenised test sample of 5 mg to 100 mg depending on the expected AOX content to a conical flask or screw-cap vial (7.2.3)

NOTE 1 Laboratories should establish their method repeatability for the range of test sample mass routinely used. Test sample mass of less than 25 mg generally gives increased repeatability standard deviation.

- b) Add 20 mg to 30 mg activated carbon (6.2) and 10 ml nitrate stock solution (6.7) to the sample. See note 2.

NOTE 2 The amount of activated carbon should be the same for all test samples, blank determinations etc.

- c) Shake for one hour by mechanical shaker (7.2.4).
- d) Filter the suspension through a filtration system (7.2.1) using nitrate washing solution (6.8). Wash the filter cake with small amounts of nitrate washing solution (6.8). Use a total volume of 25 ml to ensure complete transfer.
- e) Place the moist filter and the filter cake into the quartz sample boat (7.1.2) and proceed according to 9.3.

NOTE 3 The laboratory should ensure that the nitrate washing procedure is sufficient to remove all inorganic halides typically found in the types of samples routinely analysed. If the concentration of AOX is found to decrease with additional washing stages, then the number of nitrate washes should be increased accordingly.

9.3 Combustion

The temperature in the combustion chamber (7.1.1) shall be at least 950 °C; select other operating parameters in accordance with the manufacturer's instructions.

- a) Connect the gas supply to the combustion tube (7.1.1) and the combustion tube to the absorber (7.1.4).

Do not allow back-siphoning of the sulfuric acid (6.5) into the combustion tube; this can happen if a drop in temperature or pressure occurs.

- b) Adjust the flow of gas (6.6) to approximately 150 ml/min or follow manufacturer's instructions.
- c) Introduce the quartz sample boat (7.1.2) into the heated zone of the tube, following the manufacturer's instructions.

NOTE 1 A number of experimental variables, for example the amount of activated carbon applied, the test sample size (9.2), the dimensions of the furnace, residence time, combustion temperature, and the adjustment of the gas flow (6.6) depend on the type of apparatus and inappropriate selection may adversely affect the result.

NOTE 2 It was demonstrated that carbon to sample ratios lower than 1 (1:1) may lead to incomplete combustion of the sample/carbon mixture (seen as tailing during the argentometric detection). If this is the case, the amount of activated carbon should be raised when test samples larger than 20 mg to 30 mg are analysed. The amount of activated carbon for the corresponding blank determinations should be raised as well.

9.4 Initial calibration

9.4.1 General

Calibrate the analytical instrument (7.1) using one of the two methods described below. The calibration of the entire system is the preferred method (9.4.2). The method described in 9.4.3 is useful for checking the microcoulometric cell.

9.4.2 Calibration of the entire system

Calibrate the system by analysing at least three different levels of AOX covering the whole of the relevant working range (e.g. 0,5 µg; 5,0 µg and 10,0 µg Cl or 1,0 µg; 10,0 µg and 20,0 µg Cl) in the following way:

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- a) Transfer 20 mg to 30 mg activated carbon (6.2) to the filtration apparatus (7.2.1) and moisten it with a small amount of nitrate washing solution (6.8).
- b) Place the moist filter and the activated carbon into the quartz sample boat (7.1.2)
- c) Inject 5 µl or 10 µl of the 4-chlorophenol stock solution (6.10) or a 4-chlorophenol working solution (6.11) giving the desired amount of AOX (see table 1) and proceed with combustion according to 9.3.

Table 1 — Suggested calibration solutions

Volume added µl	Concentration of solution µg/µl	Amount of AOX µg
5	0,1	0,5
10	0,1	1,0
10	0,5	5,0
5	2,0	10,0
10	2,0	20,0

- d) Establish a linear relationship between amount of AOX analysed and instrument response:

$$N_i = i + s \cdot m_{Cl} \quad (1)$$

where:

N_i is instrument response in Coulomb (C) or instrument dependent units;

i is y -axis intercept in Coulomb (C) or instrument dependent units;

s is the slope in Coulomb (C) or instrument dependent units per µg Cl;

m_{Cl} is the amount of AOX analysed, in µg Cl.

Use the slope (s) for subsequent calculation of mass concentrations of AOX (see 10.1.1).

9.4.3 Check of argentometric measuring device

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

- a) Inject directly with a syringe (7.1.5) a known volume within the range of 5 µl to 8 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. But for practical purposes, it is important to determine the actual current yield. Obtain the correction factor by using equation (2):

$$Q = a \cdot Q_t \quad (2)$$

where:

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

Q_t is the theoretical quantity of charge for the hydrochloric acid sample, in Columb (C);

a is the correction factor.

c) Obtain the theoretical quantity of charge, Q_t , using equation (3):

$$Q_t = V \cdot c_{Cl} \cdot F \quad (3)$$

where:

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

c_{Cl} is the chloride concentration of the hydrochloric acid solution, in mol per litre (mol/l);

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

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

9.5 Recalibration

For every batch of samples, analyse at least two calibration standards with the concentrations of 20 % \pm 10 % and 80 % \pm 10 % of the established linear range and calculate the straight line from these measurements. If the straight line falls within 95 % confidence limits of the initial calibration line, the initial calibration line is assumed to be valid. If not, a new calibration line shall be established according to 9.4.

9.6 Blank determination

Suspend 20 mg to 30 mg of activated carbon (6.2) in 10 ml of nitrate stock solution (6.7) and proceed in the same way as described in 9.2. See note.

Carry out at least two blank determinations in each series and use the average blank value for subsequent calculations.

NOTE The amount of activated carbon used for the blank determination should be the same as that used for test samples.

9.7 Quality Assurance of the overall procedure

9.7.1 Duplicate determination

Analyse two individual test samples of each dried, homogenised sample submitted for analysis. Establish a control limit for the difference between results for the two sub-samples based for example on precision data given in Annex C or on laboratory precision data.

NOTE If the difference between repeated measurements of the same sample deviates more than the control limit from each other the sample should be re-homogenised (see 8.2) and the determination repeated.

10 Expression of results

10.1 Method of calculation

10.1.1 Entire system calibration (according to 9.4.2)

Calculate the mass concentration of adsorbable organically bound halogens, expressed as chloride, $Q_{Cl}(AOX)$, in mg Cl /kg dry matter, using formula (4):

$$Q_{Cl}(AOX) = \frac{N - N_0}{m_T \cdot s} \quad (4)$$

where:

N_0 is the average value for the blank, according to 9.6, in Coulomb (C) or instrument dependent units;

N is the measured value for the test sample, in Coulomb (C) or instrument dependent units;

s is the slope of the calibration curve as defined in equation (1);

m_T is the mass of the dried test sample, in grams (g).

10.1.2 Direct argentometric measurement device calibration (according to 9.4.3)

Calculate the mass concentration of adsorbable organically bound halogens, expressed as chloride, AOX), in mg Cl⁻/kg dry matter, using formula (5):

$$Q_{Cl}(AOX) = \frac{N - N_0}{m_T} \cdot \frac{M \cdot a}{F} \cdot 10^6 \quad (5)$$

where:

N_0 is the average value for the blank, according to 9.6, in Coulomb (C) ;

N is the measured value for the test sample, in Coulomb (C) ;

M is the molar mass of chloride, $M = 35,45$ g/mol;

m_T is the mass of the dried test sample, in grams (g);

a is the factor relating the theoretical to the actual quantity of charge (see equation (2));

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

10.2 Expression of results

The result shall be expressed in milligrams/kilogram (mg/kg) chloride (mg Cl⁻/kg dry matter) and reported to two significant figures.

11 Precision

The performance characteristics of the method (Annex C) data have been evaluated. Table 2 gives the resulting typical values for repeatability and reproducibility limits as well as their observed ranges. The typical value is derived from the data in Table C.2 in Annex C by taking the median value and rounding the numbers.

Table 2 — Typical values and observed ranges of the repeatability and reproducibility limits

The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.

Results of the validation of the adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r Soil and compost	27	13 - 39
Reproducibility limit, R Soil and compost	72	23 - 96
Repeatability limit, r Sludge	22	14 - 25
Reproducibility limit, r Sludge	34	22 - 36

NOTE 1. The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by $\sqrt{2}$ to obtain the corresponding typical dispersion limit and its observed range. In the example of AOX in Sludge 2 the result and its dispersion limit is 189 ± 31 mg/kg ($2 * sR = 16.5 \%$ of 189). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 158 mg/kg and lower than 220 mg/kg.

NOTE 2 The repeatability limit (r) and the reproducibility limit (R) as given in Table C.2 (Annex C) and in this table are indicative values of the attainable precision if the determination of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste test is performed in accordance with this standard [CSS99014].

NOTE 3 A limited number of materials and parameters were tested. Consequently, for other materials and parameters, performance characteristics may fall outside the limits as derived from the validation of the determination of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste.

NOTE 4 In particular for relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Table C.2 (Annex C) and this table.

12 Test report

The test report shall contain the following information:

- a) a reference to this European Standard
- b) precise identification of the sample;
- c) expression of results, according to 10.2 ;
- d) any deviation from this European Standard, and any facts 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 halogenide, suitable for the AOX determination, is commercially available. After opening of the original container, the activated carbon can become contaminated with adsorbable compounds (including organic halogens), coming from the air. The activated carbon can become inactive within five days.

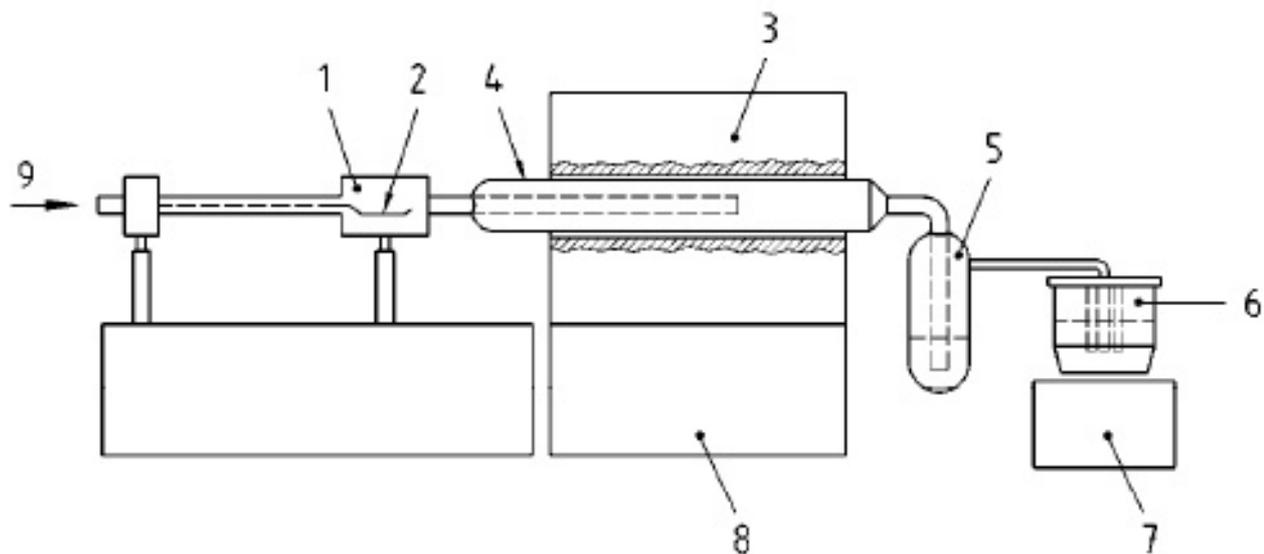
In order to keep the carbon blank low, take small quantities sufficient for one day work, for example 1,5 g to 2 g, and transfer to suitable sealed glass containers.

Use the contents of the container on the day of its opening. Discard the unused remainder at the end of the day.

Keep the remaining stock sealed. If the carbon blank is too high, use another batch after checking its blank.

Annex B
(informative)

Schematic diagram of an AOX apparatus



Key

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

Annex C (informative)

Repeatability and reproducibility data

C.1 Performance characteristics

C.1.1 Objective of the interlaboratory comparison

In a European wide interlaboratory comparison study according to ISO 5725-2, the performance characteristics of the standard “Determination of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste” were established.

C.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste was carried out with 13 - 15 European laboratories on 6 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broad as possible, because the standard will find general application across different types of soil and soil related materials. (detailed information can be found in the final report on the Interlaboratory comparison study mentioned in the Bibliography).

In the interlaboratory comparison study the following starting points were used:

The laboratory samples were all taken from one large batch of the different materials according to the normal practice. The normal size reduction and the normal repeated mixing were carried out as needed to obtain representative laboratory samples from the large batch sample (ref JRC).

Note : the samples provided for the validation should not be confused with reference samples provided for certification purposes, as the performance results obtained have to be directly applicable to daily practice (less rigorous sample preparation than for a reference material).

The experimental plan was designed by project HORIZONTAL on the basis of each laboratory being given two laboratory samples of each material to be tested. This is in accordance with ISO 5725-2.

The materials examined cover all the grain size classes to which the Determination of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0 µm to about 125 µm) and fine-grained materials (soil and compost: 0 mm to 4 mm).

Table C.1 provides a list of the types of materials chosen for testing and the selected components.

Table C.1 — Material types tested and components analysed in the interlaboratory comparison of - Determination of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste.

Grain size class	Sample code	Material type tested
Sludge (<0.5 mm)	Sludge 1	Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria
	Compost 2	Compost from Germany
	Soil 4	A sludge amended soil from Hohenheim, Germany
	Soil 5	An agricultural soil from Reading, UK

C.1.3 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table C.2).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using

its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The repeatability limit was calculated using the relationship : $r_{\text{test}} = f \cdot \sqrt{2} \cdot s_{r,\text{test}}$ with the critical range factor $f = 2$.

For instance, the repeatability limit around a measurement result of 50 mg AOX /kg is ± 13.3 mg AOX /kg (i.e ± 27 % of 50)

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value $f = 2$ used in the factor $f \cdot \sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value $f = 2$ corresponds to the usual value $k = 2$ of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). However, it may be necessary to use a larger value for f in situations as described clause 12.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor $f = 2$.

For instance the reproducibility limit around a measurement result of 50 mg AOX/kg is ± 35.9 mg AOX/kg (i.e ± 72 % of 50)

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value $f = 2$ used in the factor $f \cdot \sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value $f = 2$ corresponds to the usual value $k = 2$ of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the dispersion limit is equal to $k \cdot s_R$ with the usual value

k = 2, resulting in a dispersion limit lower than the reproducibility limit (i.e. a ratio of $\sqrt{2}$). However it may be necessary to use a larger value $f \cdot \sqrt{2}$ (or k) in some situations (notes clause 12).

In case of relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Tables Axx.2 (this means that the value chosen for the critical range factor f is larger than 2 as well as for the coverage factor k for dispersion). This is because the extreme results may have been obtained in accordance with the present standard and/or be caused by the variability within, or in between, the laboratory samples.

Table C.2 — Results of the interlaboratory comparison studies of Determination of adsorbable organically bound halogens (AOX) in soil, sludge and treated biowaste.

Matrix	Parameter	Mean mg/kg	sr	sR	r	R	p	Outliers	Total number of data
Sludge 1	AOX	215	9.21%	13.1%	55.4	78.9	15	1	67
Sludge 2	AOX	189	4.65%	8.24%	24.61	43.6	9	4	43
Compost 1	AOX	37.9	8.96%	25.9%	9.51	27.51	5	0	25
Compost 2	AOX	46.4	10.7%	25.3%	13.9	32.9	13	1	54
Soil 4	AOX	26.7	9.86%	34.2%	7.38	25.6	14	0	62
Soil 5	AOX	21.5	13.8%	31.7%	8.32	19.1	13	0	62

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit (comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs; N Number of data in statistical evaluation.

Note 1. In judging the results it is important to consider the concentration levels, at which measurements have been carried out. The choice was made to avoid spiking of samples. This implies that particularly in soil and compost low concentrations have been observed for some congeners and results below detection for other congeners. If measurement results are well below a possible critical level (regulation), between lab variabilities of up to 70 % may prove fit for purpose.

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Bibliography

- [1] Ruggedness report AOX 2007
- [2] Validation results AOX 2007