SLOVENSKI PREDSTANDARD

oSIST prEN 15171:2005

april 2005

Karakterizacija blata – Določanje organsko vezanih halogenov, sposobnih adsorpcije (AOX)

Characterization of sludges - Determination of adsorbable organically bound halogens

ICS 13.030.20

Referenčna številka
oSIST prEN 15171:2005(en)

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 15171

February 2005

ICS

English version

Characterization of sludges - Determination of adsorbable organically bound halogens

Caractérisation des boues - Détermination des composés organiques halogénés adsorbables

Charakterisierung von Schlämmen - Bestimmung von adsorbierbaren organisch gebundenen Halogenen (AOX)

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Ref. No. prEN 15171:2005: E

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Foreword

This document (prEN 15171:2005) has been prepared by Technical Committee CEN/TC 308 “Characterization of sludges”, the secretariat of which is held by AFNOR.

This document is currently submitted to the CEN Enquiry.

Introduction

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

AOX is an empirical method originally 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.

When applied to sludges, the method determines both adsorbable and occluded organically bound halogens. The term AOX is, however, conventionally used for this parameter. The AOX is a sum parameter measuring a range of different substances and gives as such no indication of the overall toxicity present in any sample, or the nature of substances present in any sample.

1 Scope

This European Standard describes an empirical method for the direct determination of an amount ranging from 5 mg/kg to approximately 6 g/kg dry matter in sludge of organically bound chlorine, bromine and iodine (but not fluorine) adsorbed and occluded to the sludge matrix. Non-volatile organically bound halogens adsorbable on activated carbon present in the aqueous phase of sludge prior to drying are included in the determination.

NOTE The upper range of the method is instrument dependent.

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 3696:1995, Water for laboratory use — Specification and test methods.

EN ISO 5667-13:1997, Water quality — Sampling — Part 13: Guidance on sampling of sludges from sewage and water treatment works.

EN 12880:2000, Characterisation of sludges — Determination of dry residue and water content.

ISO 5725:1994, Accuracy (trueness and precision) of measurement methods and results.

3 Definitions

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

3.1
adsorbable organically bound halogens (AOX)
the equivalent amount of chlorine, bromine, and iodine contained in organic compounds, expressed as chloride when determined according to this European standard.

4 Interferences

4.1 Sparingly soluble or occluded inorganic halides are included in the determination and may, if present, give a significant positive bias.

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 Loss of halogenated substances that volatilise during the drying stage at 105°C on prolonged heating.

5 Hazards

Waste and sludge samples may contain hazardous and inflammable substances. They may contain pathogens and be liable to biological action. Consequently it is recommended that these samples should be handled with special care. The gases which may be produced by microbiological activity are potentially inflammable and will pressurise sealed bottles. Exploding bottles are likely to result in infectious shrapnel

and/or pathogenic aerosols. Glass bottles should be avoided wherever possible. National regulations should be followed with respect to microbiological hazards associated with this method.

6 Principle

Addition of activated carbon to dried, homogenised sludge. Elution of inorganic halides and simultaneous adsorption of water soluble organic compounds on the activated carbon by shaking with acidified sodium nitrate solution.

Combustion of the loaded carbon / sludge mixture in an oxygen stream.

Absorption of the hydrogen halides followed by determination of the halide ions by an argentometric titration, such as microcoulometry. Expression of the result as the mass concentration of chloride.

7 Reagents

Use only reagents of recognised analytical grade and, water grade 1 in accordance with ISO 3696. The AOX content should be significantly less than the lowest AOX content to be determined.

The overall AOX contribution from water, chemicals, and gases shall be checked by measuring the total blank (see **10.4**).

7.1 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.

7.2 Nitric acid, HNO_3, p = 1,4 g/ml, 65% (m/m) solution.

7.3 Hydrochloric acid, c(HCl) = 0,100 mol/l.

The molarity shall precisely be known, since the acid is used for checking the microtitration (see **10.3.2**).

7.4 Sulphuric acid, H_2SO_4, p = 1,84 g/ml.

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

7.6 Acidified sodium nitrate, stock solution, $c(NaNO_3)$ = 0,2 mol/l

Dissolve 17 g of sodium nitrate ($NaNO_3$) in water in a 1000 ml volumetric flask, add 15 ml of nitric acid (see **7.2**), and make up to volume with water.

7.7 Sodium nitrate washing solution, $c(NaNO_3)$ = 0,01 mol/l

Pipette 50 ml of the nitrate stock solution (see **7.6**) in a 1000 ml volumetric flask, and make up to volume with water.

7.8 Methanol, CH_3OH

7.9 4-Chlorophenol, stock solution, Equivalent to AOX = 2,0 g/l

Dissolve 0,725 g of 4-chlorophenol (C_6H_5ClO) in methanol (See **7.8**) in a 100 ml volumetric flask and make up to volume with methanol (See **7.8**).

7.10 4-Chlorophenol, working solutions, Equivalent to AOX = 100 mg/l and 500 mg/l

Pipette 5 and 25 ml of 4-chlorophenol, stock solution, (see **7.9**) into two separate 100 ml volumetric flask, and make up to volume with methanol (See **7.8**). These solutions contains 0,1 and 0,5 µg/µl AOX, respectively.

7.11 2-Chlorobenzoic acid, stock solution, Equivalent to AOX = 100 mg/l

Dissolve 110,4 mg of 2-chlorobenzoic acid ($C_7H_5ClO_2$) in water in a 250 ml volumetric flask and make up to volume with water.

The stock solutions (see **7.9** and **7.11**) may be stored for at least 1 month and the working solutions (see **7.10**) for 1 week in a refrigerator in glass bottles.

8 Apparatus

8.1 Apparatus for the combustion and detection

Suitable commercial equipment should be used for the determination. This will comprise of the following.

8.1.1 Combustion apparatus

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

8.1.2 Quartz sample boat, to fit in the quartz tube.

8.1.3 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.

8.1.4 Absorber, filled with sulphuric acid (see **7.4**), to dry the gas stream and designed so that the acid does not backf1ush into the furnace.

8.1.5 Syringe, to pipette volumes of 1 µl to 10 µl of hydrochloric acid (see **7.3**) or 4-chlorophenol solutions (see **7.9** and **7.10**).

8.2 Equipment for adsorption

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

8.2.2 Low-halide 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 dedicated quartz filter for AOX determination.

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

8.2.4 Mechanical shaker for the flasks described in **8.2.3** above, equipped for example with a carrier plate.

8.3 Equipment for sample preparation

8.3.1 Porcelain evaporating dish

8.3.2 Oven with forced ventilation or natural ventilation through adjustable vents adjustable to (105 ± 5) ºC

8.3.3 Desiccator provided with a suitable desiccant

8.3.4 Analytical mill or porcelain mortar

9 Sampling and sample pre-treatment

9.1 Sampling

a) Sampling should be carried out in accordance with EN ISO 5667-13:1997

b) (b) Samples should be stored in suitable containers with an appropriate closure material such as PTFE (see Clause 5)

c) Samples to be frozen, may alternatively be stored in aluminium containers pre-cleaned by heating to 450°C for minimum 4 hours or by rinsing by a non-chlorinated solvent.

d) Samples should be kept cold (in a refrigerator) and in the dark. The sample pre-treatment should take place within 24 hours of sampling. Alternatively, samples may be frozen (-18 °C, not in glass bottles) directly after sampling and kept frozen for a maximum of one month before sample pre-treatment.

9.2 Sample pre-treatment

a) Homogenise the wet sample by shaking or stirring and transfer a sub-sample of approximately 100 g to a porcelain disc.

b) Dry the sample to constant weight at (105 ± 5) ºC as described in EN 12880:2000

c) Cool the dried sample in a desiccator, comminute and homogenise to a particle size of no more than 0,1 m in an analytical mill or porcelain mortar.

d) 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 will make the homogenisation of the dried sample easier.

10 Procedure

The test sample taken for analysis shall ideally have an AOX value within the optimal working range of the instrument, which is generally between 1 µg and 20 µg to 30 µg (absolute amount).

10.1 Adsorption and inorganic halide removal

a) As particle size distribution may be affected by settlement, ensure that the dried, ground sample is homogenised by stirring or shaking.

b) Transfer a homogenised test sample of 5 mg – 100 mg depending on the expected AOX content to a conical flask or screw-cap vial (see 8.2.3)