

# **Adsorbable organic halogens (AOX) Desk study**

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## SUMMARY

A CEN standard under development for determination of AOX in sludge is identified as a suitable basis for a horizontal standard for AOX in sludge, soil and if relevant for sediment. The AOX-parameter is not found relevant for waste. The CEN standard has been developed into a first draft horizontal standard.

The standard under development has a measurement range that is also suitable for soil. However, a number of issues need to be addressed before the standard is ready for formal vote:

- 1) Sampling and sample preparation are not sufficiently addressed in the present draft standard. It is recommended that sampling and sample preparation be covered in separate modules, general for the matrices in question.
- 2) The carbon-to-sample ratio may be critical for efficiency of the combustion step during AOX determination. It is recommended to perform a laboratory study on the effect of carbon-to-sample ratio.
- 3) The CEN standard for AOX in sludge has no tolerances for weight, volume etc. It is recommended to perform a ruggedness test in order to identify critical points in the standard and add tolerances as required.
- 4) A method evaluation interlaboratory study is needed to add precision data to the standard. It is recommended to include wet samples, as they are received in the laboratory, in the interlaboratory study.



## 1. INTRODUCTION

The objective of the project is to develop horizontal and harmonised European standards in the fields of sludge, soil and treated biowaste to facilitate regulation of these major streams in the multiple decisions related to different uses and disposal governed by EU Directives.

The revision of the Sewage Sludge Directive 86/278/EEC, the upcoming Directive on the biological treatment of biodegradable waste and the planned Soil Monitoring Directive call for standards on sampling, on hygienic and biological parameters, on methods for inorganic and organic contaminants and for mechanical properties of these materials. This project considers standards for each of these properties. When materials can not be utilised, land filling becomes important, in which case leaching becomes an issue as stipulated by Council Directive 1999/31/EC on landfill of waste.

Part of the work of the project will focus on co-normative work with an emphasis on horizontal standardisation starting from existing standards developed for the same parameter in the fields of sludge, soil and treated biowaste. Another part of the work will focus on pre-normative research required to develop standards lacking at this point and needed in the next revision of the regulations in these fields. Strong links between the Project Consortium and the relevant CEN Technical Committees (TCs) are maintained to meet these goals.

The work is split up in coherent Work Packages (WPs), which each address a main aspect of all relevant standards required or likely to be required in the Sludge, Biowaste and Landfill Directives.

The present report covers the activity for HORIZONTAL Phase I, Work package 5, Desk study for a horizontal European standard for determination of AOX in sewage sludge and comparable matrices.

Present standards prepared by CEN or ISO have been identified from the homepages of the two organisations. In addition the activities of working groups as described in work programmes are consulted. The relevant technical committees are:

CEN/TC 292 Characterisation of waste  
CEN/TC 308 Characterization of sludges  
CEN/TC 345 Soil Quality  
ISO/TC 190 Soil Quality.

## 2. EXISTING STANDARDS OR DRAFT STANDARDS

There is at present no existing standard for AOX in soil, sludge or waste. Only CEN/TC 308 (Characterisation of sludges) has under development a standard for the determination of AOX relevant to the present work.

	Reference	Title	Status
CEN/TC 292	prEN 13370:2001	Characterization of waste – Analysis of eluates - Determination of ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberable CN, F	Ratified - not relevant to the present work
CEN/TC 308	CEN/TC 308/WG 1 N0357	Characterization of sludges - Determination of AOX	Under development
CEN/TC 345		Soil quality - No work programme	-
ISO/TC 190		Soil quality - None	-

The draft standard for AOX in sludge is based on DIN 38 414, part 18:1991, Sludge and sediments - Determination of adsorbed organically bound halogens (AOX).

### 3. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

#### 3.1 Relevance to monitoring and control

AOX is a candidate for a parameter in the upcoming revision of the Sludge Directive. Since sludge may be used on soil in agriculture, soil is another potential matrix for AOX determination.

In CEN/TC 308, Austria has proposed a standard for AOX in waste, sludges and sediments, giving as justification that AOX is at present used in Austria to judge suitability of waste for landfilling /1/. However, the German mirror committee to CEN TC/292 has commented that AOX is not a suitable parameter for waste, whereas EOX (Extractable Organic Halogens) may be /2/.

CEN/TC 292/WG5 holds the view that AOX is not a relevant parameter for waste /3/.

In summary the evidence point at a potential need for determination of AOX in sludge, soil and possibly sediment but no present need in waste.

#### 3.2 Basis for a standard

As described in chapter 2, there is only one standard under development that may be used as the basis for a horizontal standard for AOX in sludge, soil and sediment. This standard under development is based on a German standard for AOX in sludge and sediment from 1991.

In CEN/TC 308/WG 1/TG 4, representatives from several countries have mentioned that they have used the German standard for many years for the determination of AOX in sludge. The technical basis for an AOX standard for sludge is therefore considered sound.

The standard under development may probably be extended to cover soil and sediment as well. However, there is a natural background of AOX in soil and probably sediment, which has to be taken into account when evaluating the usefulness of AOX in soil for monitoring and control.

Asplund *et al.* /4/ have published a method for AOX in soil, which is very similar to the standard under development for AOX in sludge. The method for soil uses a similar amount of sample, no activated carbon addition, a less intensive washing procedure and a similar combustion procedure compared to the method for sludge. Relative standard deviations are reported as less than 10%, probably as repeatability standard deviations but the publication is not clear on this point.

The concentration of AOX in soil from several countries (Sweden, The Netherlands etc.) has been reported at 30 mg/kg dry matter – 600 mg/kg dry matter /5/. The method under development for sludge has a lower limit of the measurement range of 5 mg/kg dry matter and this will probably be adequate for soil.

The standard under development covers sludge but as yet no method evaluation study for the standard has been performed. In 1989 a method evaluation study for the German standard /7/ upon which the CEN standard is based was conducted. The performance found in this study gives an indication of the level of precision to be expected for sludge. However, as the two methods are not identical it can not be assumed that their precision will be the same. Furthermore, the method evaluation study only included the AOX-parameter on dried samples

and therefore the critical drying and homogenization step was not covered. Soil and sediments were not covered.

#### 4. CRITICAL POINT AND RECOMMENDATIONS

Sampling and sample preparation for analysis are critical points in most standards for solid materials including an AOX-standard. Procedures for handling large size materials, such as stones and roots, in a soil sample and for homogenizing and drying all solid materials will be common for many parameters and it is recommended to prepare separate modules for these steps. In the standard proposed in chapter 5 these points are therefore not covered.

One point that will probably prove critical in the AOX standard is the carbon-to-sample ratio. It is appropriate to keep the amount of carbon low in order to reduce the blank but on the other hand the amount of combustible material must be sufficient to ensure complete combustion of the sample. At present there is evidence from several members of CEN/TC 398 WG 1/TG 4 that the amount of carbon is a limiting factor for combustion but there is not enough information to ensure firm guidance on the amount of carbon to be added. On the other hand, Asplund *et al.* /4/ report that addition of activated carbon is not necessary for the analysis of AOX in soil. It is therefore recommended to conduct a laboratory study on the effect of carbon-to-sample ratio. Such a study may be combined with a ruggedness test including other factors of the standard as described below.

The present standard under development for AOX in sludge has no tolerances for weight, volume, temperature and time in preparation of reagents and in the procedure. No data on ruggedness of the method are available. It is recommended to conduct a ruggedness test and, depending on the outcome of the ruggedness test, further study of critical points in the method in order to add required tolerances for the critical steps in reagent preparation and procedure.

Information on precision from method evaluation studies is not available. It is recommended to conduct a method evaluation study by interlaboratory test once the preliminary standard described in chapter 5 has been finalised based on the information obtained in the experiments recommended above. In such a study it is crucial that wet samples, as they are received in laboratories to use the method, be included to ensure that precision data covering the sample pre-treatment step become available.

## 5. DRAFT STANDARD (CEN TEMPLATE)

A draft standard has been adapted based on the standard under development in CEN/TC 308/WG 1/TG4 for AOX in sludge. The draft standard needs further development based on the laboratory investigations recommended in chapter 4. The draft standard is shown in Annex A.

## REFERENCES

- 1) CEN/TC 292/WG1 N240 E: Proposal from the Austrian mirror committee of CEN/TC 292 for a new work item for CEN/TC 292/WG5, 2000.
- 2) CEN/TC 292/WG5 N205 E: Determination of AOX. Circular, 2000.
- 3) CEN/TC 292/WG1 N0375: Minutes of the 7<sup>th</sup> meeting of CEN/TC 308/WG 1/TG 4 "organic micropollutants", Oslo, Norway, 27 March 2003.
- 4) Asplund, G., Grimvall, A. & S. Jonsson: Determination of the total and leachable amounts of organohalogens in soil, *Chemosphere* 28, pp 1467 – 1475, 1994.
- 5) Öberg, G.: The biogeochemistry of chlorine in soil, In: *The handbook of Environmental Chemistry, Vol 3, part P. The natural production of organohalogen compounds*, G. Gribble (Ed.), Springer-Verlag, pp. 43 – 62, 2003.
- 6) Tørsløv, J., Samsøe-Petersen, L., Rasmussen, J.O. & P. Kristensen: Use of Waste Products in Agriculture. Contamination Level, Environmental Risk Assessment and Recommendations for Quality Criteria. Danish Environmental Protection Agency, Environmental Project No. 366, 1997.
- 7) DIN 38 414 Part 18: Sludge and sediment (Group S). Determination of adsorbed organically bound halogens (AOX) (S 18).

APPENDIX A DRAFT STANDARD:

Determination of adsorbable organically bound halogens  
(AOX) – Solid materials