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HORIZONTAL - ORG

HORIZONTAL STANDARDS ON ORGANIC MICRO-POLLUTANTS FOR IMPLEMENTATION OF EU DIRECTIVES ON SLUDGE, SOIL AND TREATED BIO-WASTE

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SUMMARY

A ruggedness study for the proposed horizontal standard for AOX in sludge and similar matrices has been performed. The study covered the following conditions of the method:

- Type of mechanical shaker
- Weight of activated carbon added
- Volume of nitrate stock added in the first wash
- Combustion temperature
- Oxygen flow during combustion
- Residence time in the combustion chamber
- Condition of sulphuric and acetic acids

The ruggedness test shows that the proposed method is rugged for most experimental conditions. The following additions to the standard are proposed:

1. The oven temperature specified needs to be observed closely.
2. The flow of oxygen needs to be carefully optimised and controlled, preferably using reference materials.
3. The condition of acetic and sulphuric acids may influence results. Laboratories therefore need to establish the frequency of changing the acids.

The conditions for point 2 and 3 above depend on the manufacture of the equipment in question. Availability of reference materials to allow laboratories to specify conditions for their specific equipment will therefore be valuable. At present one such material is available for soil.

The study shows that the carbon-to-sample ratio is not a critical parameter, as was suggested in the desk study.

Removal of inorganic halogenide from the soil matrix is shown to be efficient.

The ruggedness study has shown the method to be useful for sludge as well as for soil. The study indicates that the method is not appropriate, at least in its present form, for biowaste. However, AOX in biowaste is not a priority and no further work on the issue is proposed.

1. INTRODUCTION

The present report covers the activity for HORIZONTAL-ORG, Work package 5, Deliverable D3.1, Ruggedness test for a horizontal European standard for determination of AOX in sewage sludge and comparable matrices.

The ruggedness test is performed for the standard identified during the desk study carried out during Phase I of the present programme /1/. In connection with the ruggedness test the efficiency of inorganic halogen removal prior to determination of AOX is also investigated.

2. MATERIALS

Samples for the ruggedness test were made available through Work package 1. The general characteristics of the samples are described in /2/. A total of 12 samples were made available. Prior to selection of samples to be used for ruggedness testing and investigation of inorganic halogens removal, an initial measurement was made to determine the level of AOX. The characteristics of the samples as described in /2/ and the AOX-levels are shown in Table 1.

Table 1 Characterisation of playground samples.

Sample id.	Sample description*	$Cl_{(XRF)}$* mg/kg	C_{org}* wgt. %	AOX mg/kg Cl
SO-1	Brown soil, Ispra, Italy	63,5	2,652	81
SO-4	Clay soil, Speyer, Germany	128	1,652	15
SO-7	Soil for rice cultivation, Vercelli, Italy	< 50	2,086	23
SO-8	Mineralised soil, Aberdeen, Scotland	< 50	3,728	(370)**
SO-9	Soil, Hagen, Germany	69	3,480	(280)**
SO-13	Terra rossa, Spain (= BCR 484)	4114	1,685	58
SO-16R	Uncontaminated soil, UK (~ Eurosoil 3R)	< 50	2,604	9
CW-1	Composted garbage, Munich, Germany	631,5	12,122	270
CW-5	Compost, Fulda, Germany	2571,5	11,450	56
S-38	Highly polluted sediment, Wuhan area, China	30702	5,693	(>14000)**
SL-4	Sewage sludge, domestic, Essen, Germany (= BCR 144)	880,5	29,035	97
SL-11	Sewage sludge, electronic industry, Turin, Italy	3892	3,177	1500

*: from /2/.
**: result may be high due to possible incomplete removal of inorganic halogen.

A soil, SO-13, was chosen for investigation of inorganic halogen removal due to the high ratio between $Cl_{(XRF)}$ and AOX.

The samples for ruggedness test were chosen to represent a wide range of concentrations, and also to represent soil and sludge. A composted waste sample was included partly because the concentration was intermediate between available soil and sludge concentrations and partly to test if the method could be expected to work for this matrix. Sample S-38, sediment, was not used because the concentration is outside the measurement range of the method. Furthermore, the sample with the lowest content of organic carbon was included since this is expected to give the highest probability for an effect of amount of carbon added during sample preparation. The samples chosen for the ruggedness test were:

SO-16R	soil	AOX ~ 9 mg/kg Cl
SO-4	soil	AOX ~ 15 mg/kg Cl
SO-1	soil	AOX ~ 81 mg/kg Cl
SL-4	sewage sludge	AOX ~ 97 mg/kg Cl
CW-1	composted garbage	AOX ~ 270 mg/kg Cl
SL-11	sewage sludge	AOX ~ 1500 mg/kg Cl

3. DESIGN OF RUGGEDNESS TEST

The ruggedness test was performed according to the design described by Youden & Steiner /3/. This design investigates the effect of seven experimental conditions. The conditions chosen are described in Table 2.

Table 2 Conditions for ruggedness test.

Factor	**Letter**	**Value for capital letter**	**Value for lower-case letter**
Mechanical shaker	A, a	Reciprocating shaker	Rotary shaker
Weight of activated carbon	B, b	15 mg	35 mg
Volume nitrate stock (6.6) for initial wash	C, c	8 mL	12 mL
Combustion temperature	D, d	850°C	1050°C
Oxygen flow during combustion	E, e	45 mm (flowmeter) ≈ 170 mL/min	55 mm (flowmeter) ≈ 250 mL/min
Residence time in combustion chamber	F, f	2 min	20 min
Condition of sulphuric acid and acetic acid	G, g	Fresh - used for less than 4 determinations of solid samples	Used for 8 or more determinations of solid samples

These experimental factors were combined in a total of eight experiments for each of the six samples chosen for the ruggedness test (see Chapter 2). In order to achieve the difference of "age" for sulphuric acid and acetic acid needed to investigate the effect, each batch of experiments was performed in the following sequence:
First four experiments for the ruggedness test ("fresh" acids – condition G),
Then four experiments to determine the efficiency of chloride removal, and
Finally four experiments of the ruggedness test ("old" acids – condition g).

All experiments in one batch of analyses were performed using the same calibration curve. Calibration was thus not repeated as experimental conditions were changed.

Each determination in the ruggedness test was performed according to the design described in Table 3.

Table 3 Design for the eight experiments of the ruggedness test.

	Values for factors in determination no.							
Experimental factor	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Mechanical shaker	A	A	A	A	a	a	a	a
Weight of activated carbon	B	B	b	b	B	B	b	b
Volume nitrate stock	C	c	C	c	C	c	C	c
Combustion temperature	D	D	d	d	d	d	D	D
Oxygen flow	E	e	E	e	e	E	e	E
Residence time (combustion)	F	f	f	F	F	f	f	F
Condition of acids	G	g	g	G	g	G	G	g

4. RESULTS AND DATA ANALYSIS FOR RUGGEDNESS TEST

The results for all determinations in the ruggedness test are shown in appendix A.

In addition to the measurements, it was observed that the combustion temperature of 850°C led to incomplete combustion, leaving charred fragments of sample in the sample boat. 850°C is below the minimum temperature specified in the procedure and it is therefore important that the procedure be followed closely in this respect. The effect on the results is described below.

The effects of the experimental conditions are shown by average differences between results of the determinations for each sample. The differences are calculated as follows:

Factor	Average difference for determinations no.
Mechanical shaker	(1+2+3+4) - (5+6+7+8)
Weight of activated carbon	(1+2+5+6) - (3+4+7+8)
Volume of nitrate stock	(1+3+5+7) - (2+4+6+8)
Combustion temperature	(1+2+7+8) - (3+4+5+6)
Oxygen flow during combustion	(1+3+6+8) - (2+4+5+7)
Residence time in combustion chamber	(1+4+5+8) - (2+3+6+7)
Condition of sulphuric and acetic acids	(1+4+6+7) - (2+3+5+8)

These differences are shown in appendix A. As would be expected the size of the differences depends on the concentration of AOX in the samples. For further data analyses the differences relative to average sample concentration are used (see Table 4).

Table 4 Relative differences (AOX, mg/L Cl) related to experimental conditions

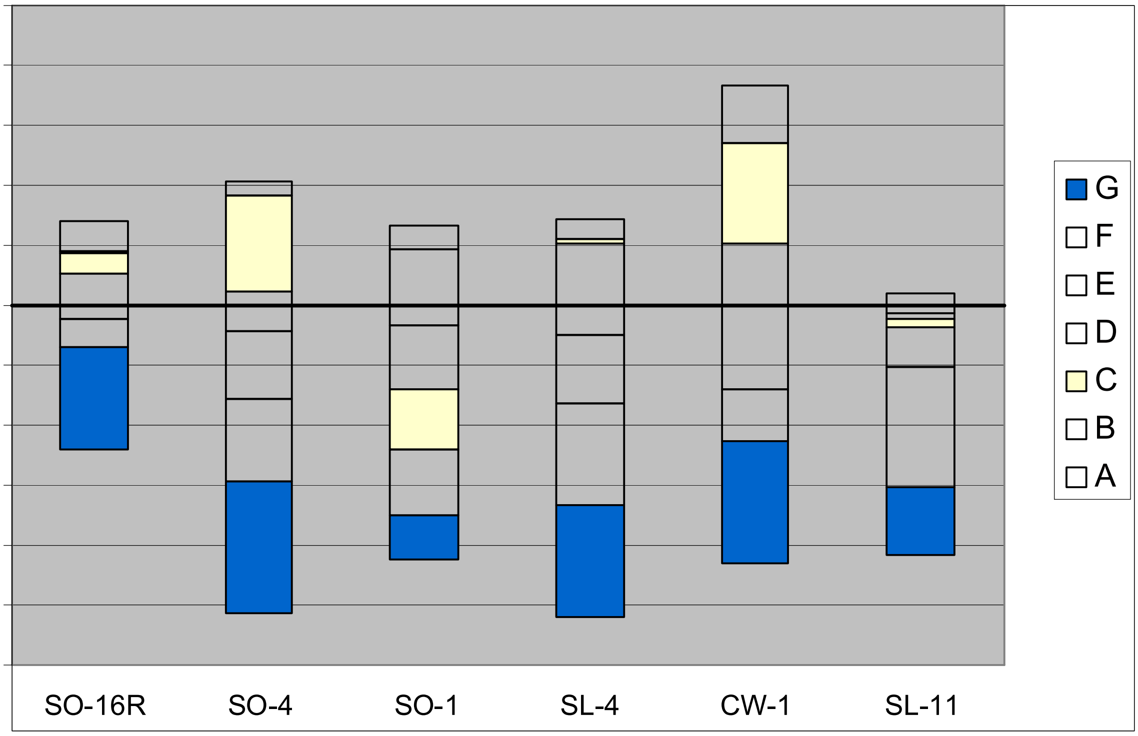
Factor	SO-16R	SO-4	SO-1	SL-4	CW-1	SL-11
Mechanical shaker	-0,047	0,044	-0,065	-0,098	0,001	-0,027
Weight of carbon	0,108	-0,088	-0,218	0,207	0,204	-0,023
Volume nitrate stock	0,063	0,321	-0,197	0,014	0,336	-0,023
Combustion temp.	-0,095	-0,228	0,189	-0,227	-0,277	-0,132
Oxygen flow	0,012	-0,268	-0,218	-0,341	-0,173	-0,403
Residence time	0,094	0,052	0,079	0,065	0,193	0,041
Condition of acids	-0,339	-0,439	-0,147	-0,372	-0,407	-0,222

Inspection of Table 4 shows that for the choice of mechanical shaker, weight of activated carbon and volume of nitrate stock solution the sign of the differences spilt more or less evenly between plus and minus. This implies that the differences observed are due to random variations. This is not the case for combustion temperature, flow of oxygen in the combustion chamber, residence time of sample boat in the combustion chamber and the condition of acetic and sulphuric acids.

The data are further illustrated in Figure 1. The figure illustrates that two factors, the flow of oxygen and the condition of acids, give the main contribution to differences. The combustion temperature follows. The remaining factors give either small effects or effects that vary randomly between positive and negative values.

In the desk study /1/ was mentioned that the carbon-to-sample ration may be critical. Figure 1 shows that the amount of carbon added has an effect that varies between positive and negative. The effect, if present, would be expected to be most pronounced for samples with low content of organic carbon (SO-4) and least pronounced with samples with high content of organic carbon (SL-4). The data show no such correlation. It is therefore concluded that the carbon-to-sample ratio is not a critical parameter.

The figure also shows that for the sample CW-1, composted waste, all factors except the type of mechanical shaker (A) give large effects. This is taken to indicate that the procedure is not suitable for composted waste. Composted waste is therefore not included in the discussion. It should be noted that conclusions would be the same if composted waste had been included.



A: type of mechanical shaker; B: Weight of activated carbon; C: Volume of nitrate stock;
D: Combustion temperature; E: Oxygen flow during combustion;
F. Residence time in combustion chamber; G: Condition of sulphuric and acetic acids.

Figure 1 Relative effects of experimental conditions for AOX in solid samples.

The samples are order in Figure 1 by increasing concentration of AOX. It is evident that concentration of AOX in the samples is not connected to the relative difference observed. The method is therefore not limited by concentration, within the range of concentrations tested.

Combustion temperature:
A higher combustion temperature tends to give a higher measurement value. Temperatures tested are 850°C and 1050°C. This is consistent with the observation of charred material in the sample boat after combustion at 850°C. The effect is less evident than for oxygen flow and condition of acids.

Oxygen flow:
Higher oxygen flow also tends to give higher measurement values. The two flows tested were 170 mL/min and 250 mL/min. The effect is in the same order of magnitude as for the condition of acids.

Residence time in combustion chamber:
A long residence time of the sample boat in the combustion chamber seems to result in lower measurement values. Residence times tested are 2 minutes and 20 minutes. The effect is small compared to combustion temperature, oxygen flow and condition of acids. During measurements it was observed that the reading had returned to the baseline even after the short residence time. The effect is therefore considered negligible.

Condition of acetic acid and sulphuric acid:
The tests show that measurements clearly increase as more samples are measured without change of acids. The effect is consistent for all six samples and is the largest of the effects observed. The two conditions tested are "acid used for four samples or less" and "acid used for eight samples or more".

The ruggedness test has thus pointed to two factors that are most likely to cause variation in measurement of AOX in soil and sludge by the proposed method: The condition of acetic and sulphuric acids in the AOX equipment, and the flow of oxygen during combustion. In addition the test has shown that the minimum combustion temperature specified in the method must be observed.

5. EFFICIENCY OF INORGANIC HALOGEN REMOVAL

Leaching of inorganic halogens from solid samples was tested by measuring "AOX" in soil SO-13 by the standard procedure, and the standard procedure minus one, two or all washing steps with nitrate washing solution. Each step was tested in duplicate and in two separate batches. The results are shown in appendix B.

The experiments were performed in response to a comments for the desk study /1/ suggesting further laboratory work to investigate the efficiency of the nitrate washing stage.

The soil is high in total chorine (XRF) compared to AOX.

The average of all measurements for each procedure is shown in Figure 2 together with "AOX" measured in the soil as it is, with no washing. The total content of chlorine in SO-13 as reported in /2/ is considerably higher, 4114 mg/kg.

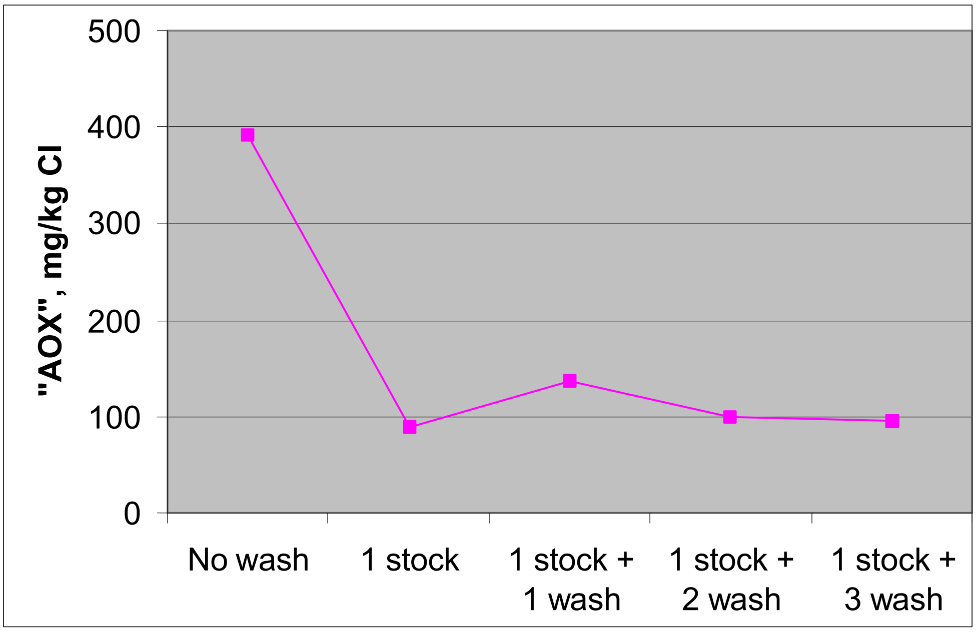


Figure 2 Efficiency of inorganic halogen removal in by the washing procedure.

Figure 2 shows clearly that after the first wash the amount of AOX measured remains constant, indicating that inorganic halogenide is removed by one wash. This is consistent with comments from German laboratorier (R. Leschber, personal communication) that the amount of washing in the present proposal for an AOX standard is excessive.

6. CONCLUSIONS

The ruggedness test showed that the proposed method is rugged for most experimental conditions. However, the oven temperature specified needs to be observed closely. Furthermore, other conditions of the equipment may influence the results: the flow of oxygen and the condition of acetic and sulphuric acids. Laboratories therefore need to control these conditions. The control will depend on the manufacture of the equipment in question. Availability of reference materials to allow laboratories to specify conditions for their specific equipment will therefore be valuable. At present one such material is available for soil.

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2 Gawlik, B.M., F. Bo, F. Sena, L. Roncari, G. Locoro & R. Vivian: Characterisation of "Playground" samples to be used in the context of Project "Horizontal". Part 1: Inorganic parameters. SWCR-Report No 03/07/2004.

3 Youden, W.J. & E.H. Steiner: Statistical manual of the AOAC, Published by AOAC International. 1975.

APPENDIX A RESULTS OF EXPERIMENTS IN RUGGEDNESS TEST

Sample: Determination no.	SO-16R	SL-4	SO-4	CW-1	SO-1	SL-11
	Concentration of AOX (mg/kg Cl) measured					
1	30,35	215,8	43,34	579,0	79,60	1178
2	36,09	435,2	64,17	610,5	133,6	2359
3	38,18	328,8	87,11	755,8	90,44	1832
4	27,37	336,1	59,78	523,5	129,3	2309
5	46,20	574,9	98,85	1107	106,6	2705
6	29,83	301,0	31,62	423,0	78,88	1453
7	24,69	273,5	59,57	439,5	126,8	1980
8	37,60	301,8	53,51	496,2	149,78	1751
Average for all determinations	33,8	346	62,2	617	112	1946

Experimental conditions for each determination are described in Chapter 3.

From the above data the average of results for conditions denoted by lower case letters are subtracted from the average of results for conditions denoted by capital letters. For each condition the differences between the two averages are shown below:

Sample: Factor	SO-16R	SL-4	SO-4	CW-1	SO-1	SL-11
	Differences, AOX (mg/kg Cl)					
Mechanical shaker	-1,5825	-33,8375	2,715	0,775	-7,28	-52,75
Weight of carbon	3,6575	71,6875	-5,495	126,125	-24,41	-44,25
Volume nitrate stock	2,1325	4,7125	19,95	207,025	-22,03	-44,25
Combustion temp.	-3,2125	-78,6125	-14,195	-171,025	21,14	-257,75
Oxygen flow	0,4025	-118,088	-16,7	-106,625	-24,4	-784,75
Residence time	3,1825	22,5375	3,25	119,225	8,89	79,75
Condition of acids	-11,4575	-128,563	-27,33	-251,125	-16,46	-431,75

APPENDIX B RESULTS OF EXPERIMENTS FOR TESTING REMOVAL OF INORGANIC CHLORINE

		AOX, mg/kg Cl	
	Sample:	SO-13	SO-13
Washing procedure	Date		
Sample measured without washing		391,9	
1 stock		99,84	77,32
1 stock + 1 wash	18-02-2005	109,1	124,2
		138,4	175,8
1 stock + 2 wash	21-02-2005	89,70	91,37
		91,41	125,1
1 stock + 3 wash	15-02-2005	84,16	*
		103,3	99,63

*: sample lost