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

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**D3.1 European standard method for determination of AOX in sewage sludge and comparable matrices - Ruggedness testing**

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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 repeatability of the measurement is adversely affected when using sub-samples for analysis at the low end of the weight range specified in the standard. Very low sub-sample weights should be avoided if possible, and the increased uncertainty must be taken into account if low sub-sample weights are used.

The ruggedness 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. It is also shown that a batch washing procedure gives comparable results to washing the soil/carbon mixture on a filter. Since the latter is the simpler process the draft AOX-standard will be changed to washing on the filter.

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. Furthermore, the repeatability and the influence of the amount of subsample taken for analysis on repeatability is 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 samples used in the investigations.

Sample id.	Sample description*	Grain size mm	Cl <sub>(XRF)</sub> * mg/kg	C <sub>org</sub> * wt. %	AOX-level mg/kg Cl
SO-1	Brown soil, Ispra, Italy	0,125*	63,5	2,652	80
SO-4	Clay soil, Speyer, Germany	< 0,125*	128	1,652	20
SO-7	Soil for rice cultivation, Vercelli, Italy	-	< 50	2,086	20
SO-8	Mineralised soil, Aberdeen, Scotland	-	< 50	3,728	(400)**
SO-9	Soil, Hagen, Germany	0,125*	69	3,480	(300)**
SO-13	Terra rossa, Spain (= BCR 484)	< 2*	4114	1,685	60
SO-16R	Uncontaminated soil, UK (~ Eurosoil 3R)	< 2*	< 50	2,604	10
CW-1	Composted garbage, Munich, Germany	-	631,5	12,122	300
CW-5	Compost, Fulda, Germany	-	2571,5	11,450	60
S-38	Highly polluted sediment, Wuhan area, China	-	30702	5,693	(>14000)**
SL-4	Sewage sludge, domestic, Essen, Germany (= BCR 144)	< 0,125*	880,5	29,035	100
SL-11	Sewage sludge, electronic industry, Turin, Italy	< 0,125*	3892	3,177	2000
SOLID-9A	Contaminated soil from soil remediation plant	< 1			
SOLID-9B	Contaminated soil from soil remediation plant	< 1			

\*: 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<sub>(XRF)</sub> 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 ~ 10 mg/kg Cl
SO-4	soil	AOX ~ 20 mg/kg Cl
SO-1	soil	AOX ~ 80 mg/kg Cl
SL-4	sewage sludge	AOX ~ 100 mg/kg Cl
CW-1	composted garbage	AOX ~ 300 mg/kg Cl
SL-11	sewage sludge	AOX ~ 2000 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.

Experimental factor	Values for factors in determination no.							
	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

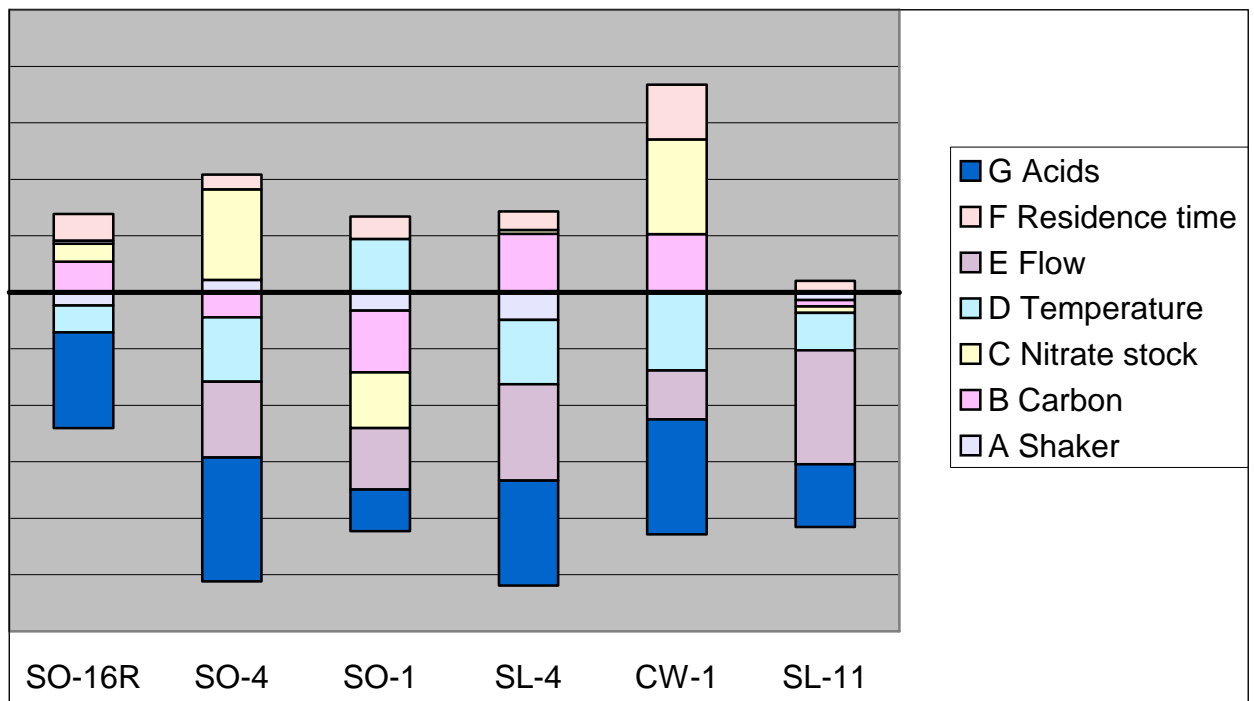
Factor	SO-16R	SO-4	SO-1	SL-4	CW-1	SL-11
Mechanical shaker	-0,047	0,044	-0,065	-0,098	0,001	-0,027
Weight of carbon	0,108	-0,088	-0,218	0,207	0,204	-0,023
Volume nitrate stock	0,063	0,321	-0,197	0,014	0,336	-0,023
Combustion temp.	-0,095	-0,228	0,189	-0,227	-0,277	-0,132
Oxygen flow	0,012	-0,268	-0,218	-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. However, for the three soil samples tested the effect of volume of nitrate stock solution is large compared to sludge samples.

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.

**Type of mechanical shaker:**

The type of mechanical shaker has only a small effect on AOX-results and the effect varies in sign. It is therefore concluded that the type of mechanical shaker does not have significant effect on the AOX-results.

**Weight of activated carbon:**

The effect of the weight of activated carbon is small relative to effects of other experimental conditions and the sign of the effect is evenly distributed between plus and minus. It is therefore concluded that the weight of activated carbon has insignificant effect on AOX-results.

**Volume of nitrate stock solution:**

The volume of nitrate stock solution gives an effect that varies both in magnitude and sign. The three soil samples show larger effects than the sludge samples, although also with both positive and negative values. The probability is therefore that the volume of nitrate stock solution has no effect within the volumes tested (from 8 to 10 mL) but to rule out a possible effect on soil samples, the effect was tested further in a separate experiment for soil samples (see Chapter 5).

**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. The effect was tested in a separate experiment with five different temperatures (see Chapter 5).

**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. The possible effect was tested in a separate experiment (see Chapter 5).

**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 measurement values 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”.

However, scrutiny of the output from the AOX instrument showed erratic peak shapes with tailing peaks. A test using only a 10 µg standard solution also showed increasing values after a limited load of organic halogen to the instrument. All experiments were performed on an instrument that apparently worked well for periods of time but still did require frequent repair for the manufacturer’s service engineer. An artefact was therefore suspected and the test using a 10 µg standard solution was repeated on another instrument.

The repeated test confirmed that the apparent increase in concentration as the load of AOX on the sulphuric acid and microcoulometric cell increased was an artefact caused by an instrument in sub-optimal condition. This condition may be identified by excessive drift in calibration as well as anomalous peak shapes.

#### 4.1 Conclusion on ruggedness test

The ruggedness test has pointed to the flow of oxygen during combustion as the factor that is most likely to cause variation in measurement of AOX in soil and sludge by the proposed method. The volume of nitric acid stock solution may have an effect on soil samples. In



addition the test has shown that the minimum combustion temperature specified in the method must be observed.

The three possible effects were studied in separate experiments to determine the size of the effect and to prepare the necessary specifications to be added to the procedure (see Chapter 5).

## 5. INVESTIGATION OF SPECIFIC CONDITIONS

### 5.1 Volume of nitrate stock solution

The possible effect on soil samples of the volume of nitrate stock solution used for washing of inorganic halogen from the sample was investigated using eight different soil samples. The effect was tested in four different batches, two with low volume of nitrate stock solution and two with high volume. The results are shown in appendix C. A summary of the results is shown in Table 5.

Table 5 Effect of volume of nitrate stock solution.

<b>Volume of nitrate stock solution</b>	<b>8 mL</b>	<b>12 mL</b>	
<b>Sample</b>	Average, mg/kg Cl	Average mg/kg Cl	Difference, mg/kg Cl
SOLID9A-146	26,6	24,6	-2
SO-7	31,0	30,6	-0,4
SO-16R	31,2	31,35	0,15
SO-4	53	54,75	1,75
SO-13	96	102	6
SO-9	98,55	102	3,45
SO-1	115	115	0
SO-8	115,5	114	-1,5
Average difference			0,93

The average values shown in Table 5 are from results of measurements in two separate batches. The difference between the averages have three negative and five positive values. This indicates that the effect is random. The samples are ordered according to increasing concentration of AOX. There is no indication that the difference observed increases with increasing concentration. The average difference is 0,93 mg/kg Cl, which is insignificant compared to the repeatability of the AOX measurements, see Chapter 7.

It is thus concluded that a variation of volume of nitrate stock solution between 8 mL and 12 mL does not affect the results of AOX measurement on soil samples significantly. Since the ruggedness test showed no effect on sludge samples there is no reason to add a specification of acceptable variation on volume of nitrate stock solution to the horizontal standard for AOX in soil and sludge.

### 5.2 Combustion gas flow

The possible effect of flow of combustion gas was investigated at the flow setting (reading on flow-meter) recommended by the instrument manufacturer and at 10% deviation on either side of the setting. The investigation was done using one soil sample, one sludge sample and a 5 µg standard solution. The samples were analysed 4 times for each flow setting. Results can be seen in appendix D and results of statistical analyses of the data are shown in Table 6.

Table 6 Effect of variations in flow of combustion gas

Flow, mL/min		170	210	250		
Sample	Unit	Average $\pm$ std.dev.			Std. dev, analytical	Std. dev., flow
SO-4	mg/kg Cl	49,4 $\pm$ 1,31	47,1 $\pm$ 3,38	49,9 $\pm$ 1,57	2,28	2,56
SL-4	mg/kg Cl	288,0 $\pm$ 5,10	295,5 $\pm$ 7,85	300,8 $\pm$ 7,23	6,83	9,13
5 $\mu$ g standard	$\mu$ g Cl	4,57 $\pm$ 0,146	4,32 $\pm$ 0,057	4,80 $\pm$ 0,223	0,157	0,266

Table 6 shows no trend in level and variability of the data at the three flow settings investigated. The analytical variability and variability according to flow of combustion gas were found by analysis of variance. These are also shown in Table 6. An F-test (95% confidence level) was used to test if the variability due to changes in flow settings was larger than the analytical variability. The test value was in all three cases smaller than the critical value and variations in flow therefore has no significant effect on the results within the range of settings investigated.

The conclusion of the visual inspection of the data as well as statistical analyses is that the flow does not affect the results within the flow settings investigated, i.e. the setting recommended by the instrument manufacturer  $\pm$  10%. The effect seen in the ruggedness test is large compared to the effect of other experimental parameters investigated but the size of the effect is still negligible. There is therefore no reason to add a specification for flow of combustion gas to the standard for AOX.

### 5.3 Temperature in combustion chamber

The ruggedness test indicated that a temperature below the minimum temperature required in the draft AOX standard caused lower results. The effect of temperature was therefore investigated at 5 settings around 950°C as required in the draft standard. At each temperature four measurements were made of the soil and sludge samples as well as two measurements of the 5  $\mu$ g standard. The data are found in appendix E and results of data analysis are shown in Table 7.

Table 7 Effect of temperature in combustion chamber

Temperature in combustion chamber		1050	1000	950	900	850	
Sample	Unit	Average $\pm$ std. dev.					Std. dev, analytical
SO-1	mg/kg Cl	115,5 $\pm$ 2,16	113,5 $\pm$ 2,08	111,5 $\pm$ 3,30	116,5 $\pm$ 1,71	99,35 $\pm$ 8,37	2,19
SO-4	mg/kg Cl	52,1 $\pm$ 1,88	50,8 $\pm$ 1,11	48,7 $\pm$ 1,73	49,2 $\pm$ 1,41	47,0 $\pm$ 1,59	2,28
SL-4	mg/kg Cl	305,5 $\pm$ 7,55	301,3 $\pm$ 6,65	287,5 $\pm$ 11,2	291,0 $\pm$ 10,9	287,3 $\pm$ 33,5	6,83
5 $\mu$ g standard	$\mu$ g Cl	4,97 $\pm$ 0,162	4,99 $\pm$ 0,247	4,68 $\pm$ 0,106	4,78 $\pm$ 0,346	4,58 $\pm$ 0,551	0,157

The analytical standard deviations shown in Table 7 are not based on data in appendix E since lower temperature seems to result in higher standard deviations. The analytical standard deviations are therefore taken from repeatability experiments, see Chapter 7.

Visual inspection of the data in Table 7 indicates that low combustion temperature gives lower measured values as well as higher standard deviations. The sizes of the measured standard deviations were tested against the expected analytical standard deviations using an F-test at 95% confidence level. The test showed that at 850°C the standard deviations were significantly higher than expected for all samples except the soil sample, SO-4.

The averages at temperatures between 850°C and 1000°C were compared to the average obtained at 1050°C for each sample. The comparison was done using Student's t-test et 95% confidence level. The test showed significant difference between averages at 1050°C and 850°C for the three soil and sludge samples but - as would be expected - not for the 5 µg standard. The sludge sample, SL-4, also has significantly lower average at 950°C but not at 900°C. The average values are visualised in Figure 2.

An additional indication that 850°C in the combustion chamber is insufficient is that an anomalous peak shape was observed for some of the measurements (see appendix E).

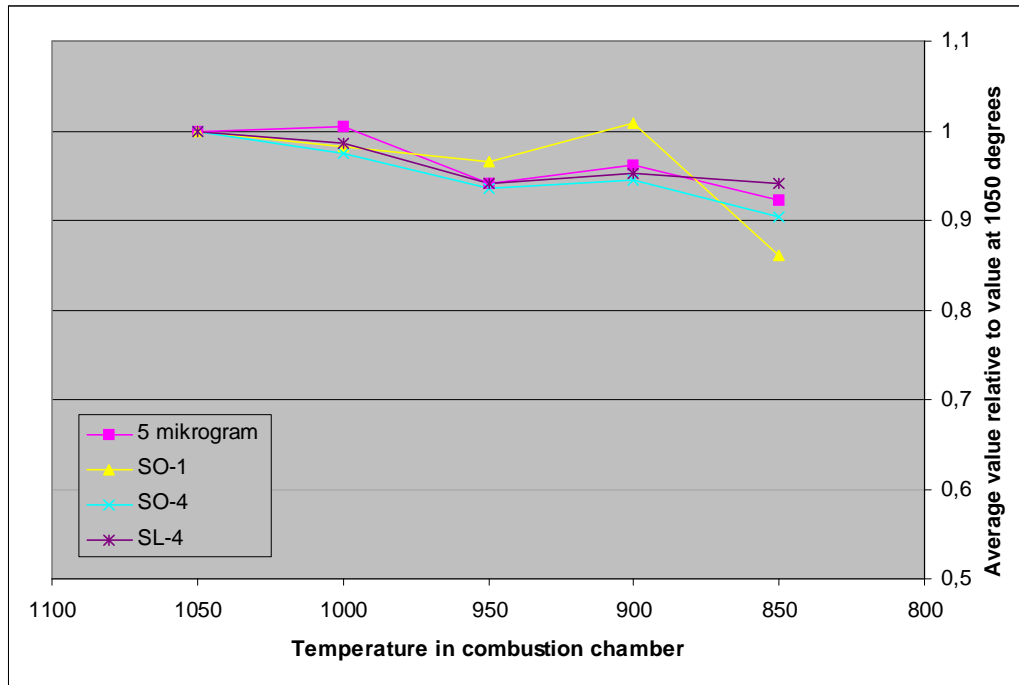


Figure 2 Concentrations relative to measured value at 1050°C as a function of temperature in combustion chamber.

The figure indicates that even at 950°C the measured values decrease but the effect is not statistically significant.

The investigations show that the present requirement for a minimum temperature of 950°C in the combustion chamber must be strictly adhered to. A cautionary note to this effect will be added in the AOX standard.

## 6. EFFICIENCY OF INORGANIC HALOGEN REMOVAL

### 6.1 First draft AOX standard

The first draft of the AOX standard included a procedure where washing was performed in the extraction vessel and the soil and carbon transferred to a filter after the final washing step. The efficiency of this washing procedure was tested in response to a comment for the desk study /1/ suggesting further laboratory work to investigate the efficiency of the nitrate washing stage.

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

The average of all measurements for each procedure is shown in Figure 3 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.

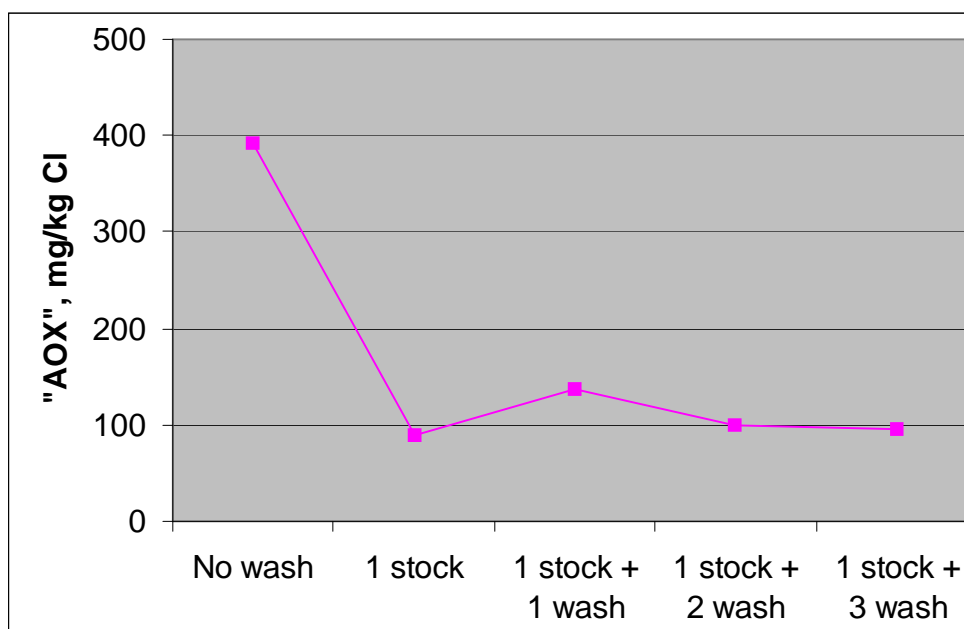


Figure 3 Efficiency of inorganic halogen removal in by the washing procedure.

Figure 3 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 laboratories /R. Leschber, personal communication/ that the amount of washing in the present proposal for an AOX standard is excessive.

### 6.2 Second draft AOX standard

The first draft AOX standard was sent for comment in the national standardisation bodies. Several comments suggested that the nitrate washing procedure was unnecessarily cumbersome. It was therefore suggested that a washing procedure at present incorporated in the DIN-standard

for AOX in sludge /4/ be used instead. In this procedure the soil and activated carbon is transferred to a filter after the first wash with nitrate stock solution, and subsequent washing with nitrate washing solution is performed on the filter.

In order to test the advisability of this change the original procedure was compared to the DIN-procedure by duplicate measurement of 13 different samples by each of the two washing procedures. The data are found in appendix F and Figure 4 illustrates the result by a plot of the average using the first draft AOX-standard versus the average using washing according to the DIN-standard.

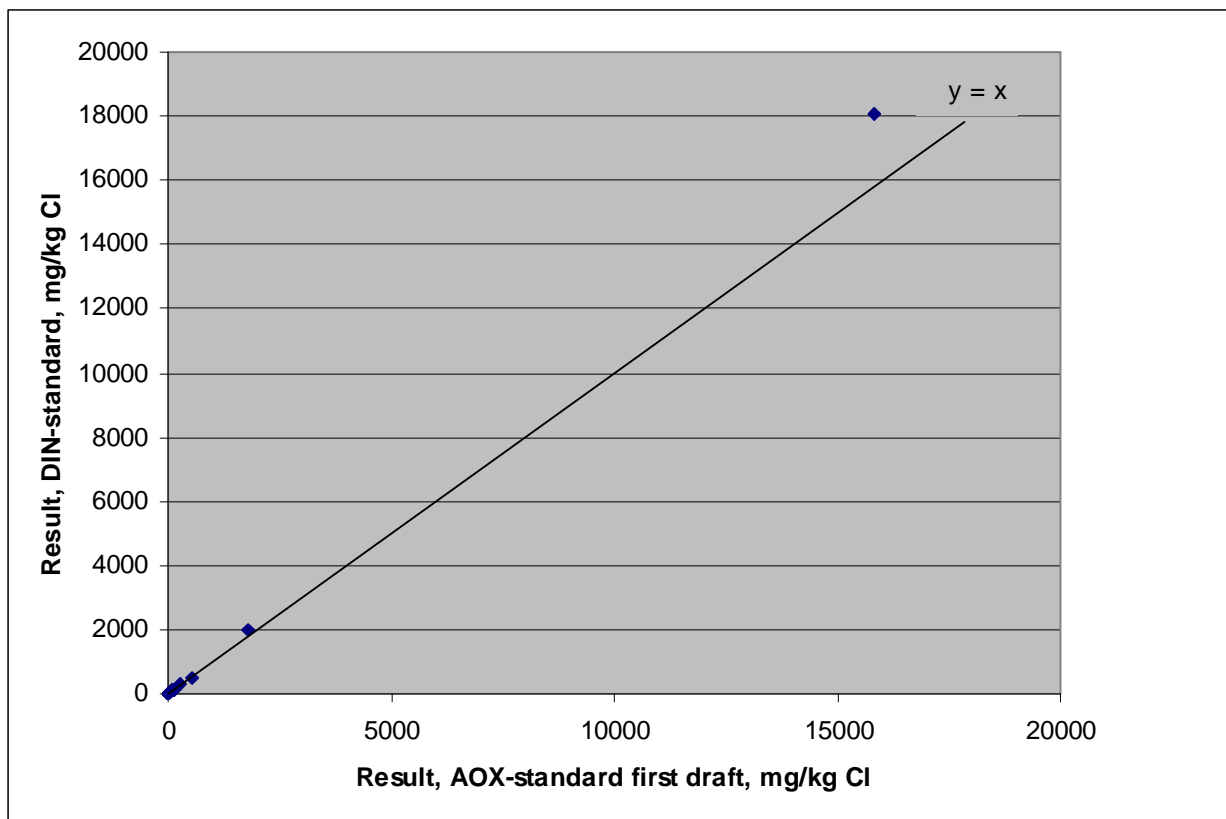


Figure 4 Comparison of washing procedures using the first draft AOX-standard and the DIN-standard.

The results from the two washing procedures fit very well around the line  $y = x$ . The average relative difference between the washing procedures is 2.5%, which is not significantly different from zero (t-test, 95% confidence level).

It is concluded that the two washing procedures do not differ and the DIN washing procedure is therefore incorporated into the second draft AOX-standard.

## 7. REPEATABILITY

The AOX standard uses only between 10 and 100 mg of sub-sample for each measurement. Homogeneity of the sample is therefore of concern and there is a risk that repeatability may be unacceptable when using sub-samples in the low end of the weight range. An experiment to illustrate the effect of sub-sample weight was therefore conducted. In addition data from examination of the effect of combustion gas flow have been used. This is possible as the flow was shown to have no effect within the range of conditions tested, see Chapter 5.2. The data used to assess repeatability are shown in appendix G.

The standard deviation is shown as a function of sub-sample weight in Figure 5. The data cover four soil and one sludge sample, some of which have been analysed at more than one weight of sub-sample.

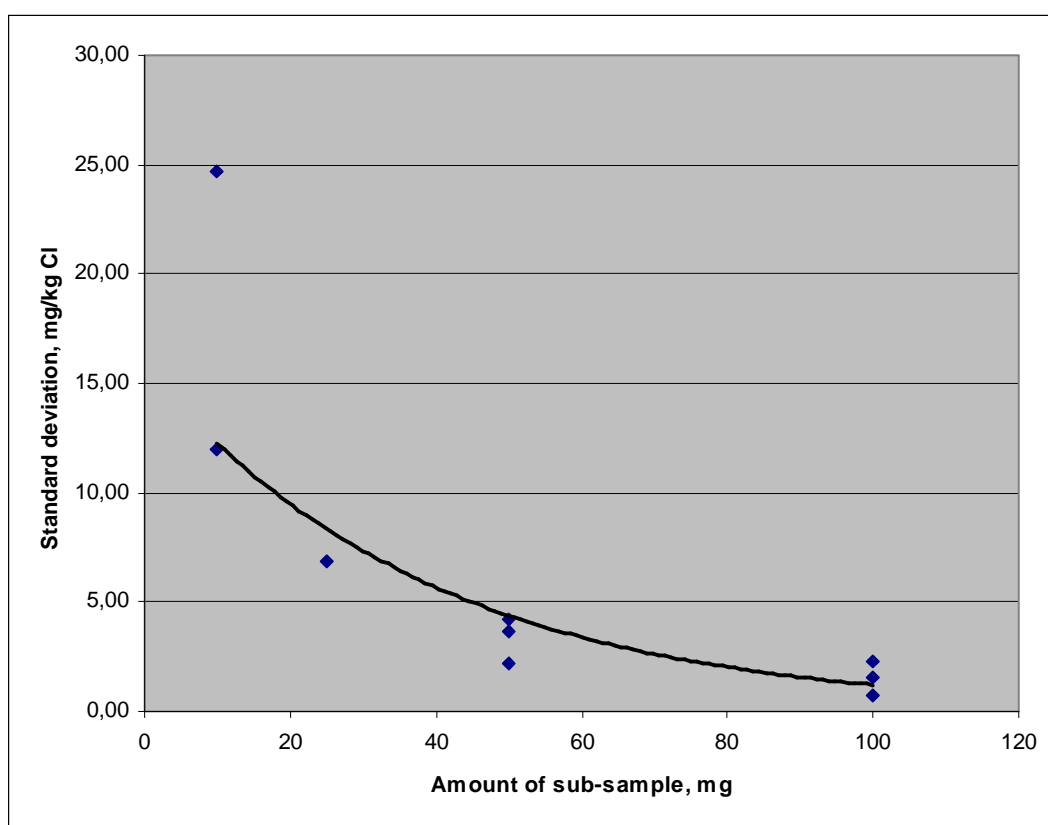


Figure 5 Standard deviation for soil and sludge samples as a function of the amount of sub-sample taken for analysis.

The figure shows that the standard deviation increases with decreasing amount of sub-sample. The standard deviation is especially high at a sub-sample weight of 10 mg. Both samples used at this sub-sample weight had been crushed and sieved to a particle size < 0,125 mm. The standard deviations relative to AOX-content are 10 – 20% at 10 mg sub-sample weight (appendix G). Relative standard deviations at all other weights of sub-sample are in the range 1 – 5%. The very low sub-sample weights should therefore not be used unless the upper end of the calibration curve is exceeded, and if used the increase in uncertainty must be taken into account and reported.

A note to this effect will be added to the AOX-standard.

The high standard deviation at low sub-sample weight might also be due to a low amount of AOX in the sample and therefore higher uncertainty on the instrumental measurement. Inspection of the data in appendix G shows that the standard deviation varies randomly with the amount of AOX in the sub-sample. Furthermore, the standard deviations seen for pure standards are much lower than for the soil and sludge samples. The instrumental measurement therefore does not contribute significantly to the repeatability of the AOX-measurements.



## 8. CONCLUSIONS

The ruggedness test and additional detailed studies have shown that the proposed method is rugged for most experimental conditions. However, the oven temperature specified needs to be observed closely.

The type of mechanical shaker, weight of activated carbon and residence time in the combustion chamber were identified in the ruggedness study itself as contributing insignificantly to the variability of AOX measurements. The condition of the acetic and sulphuric acids in the AOX instruments was at first indicated as a major contributor to variability. However, further investigation showed this to be the effect of an instrument in sub-optimal condition with excessive drift in calibration as well as anomalous peak shapes. No further investigations were therefore performed for this experimental condition. The following experimental conditions were tested in separate experiments specific for each condition: volume of nitrate stock solution, flow of combustion gas and combustion temperature.

The volume of nitrate stock solution as well as the flow of combustion gas was shown to have insignificant effect on the measurements. The combustion temperature must be at least 950°C as required in the standard, as lower temperature gives both lower results and higher standard deviation. Availability of reference materials to allow laboratories to test conditions for their specific equipment will 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. It is also shown that a batch washing procedure gives comparable results to washing the soil/carbon mixture on a filter. Since the latter is the simpler process, the draft AOX-standard will be changed to washing on the filter.

The repeatability standard deviation was shown to be very high (10 – 20%) using sub-sample weights for analysis in the low end of the range specified in the standard. From 25 mg of sub-sample the repeatability standard deviation was in the range 1 – 5%. A cautionary note on low sub-sample weights will therefore be added to the standard.

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.

## REFERENCES

- 1 Lund, U: Horizontal. Adsorbable organic halogens (AOX). Desk study. May 2004.
- 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.
- 4 DIN 38 414 Part 18: Sludge and sediments (Group S), Determination of adsorbed organically bound halogens (AOX) (S18).

## APPENDIX A RESULTS OF EXPERIMENTS IN RUGGEDNESS TEST

Determination no.	Concentration of AOX (mg/kg Cl) measured					
	Sample: SO-16R	SL-4	SO-4	CW-1	SO-1	SL-11
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:

Factor	Differences, AOX (mg/kg Cl)					
	Sample: SO-16R	SL-4	SO-4	CW-1	SO-1	SL-11
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**

	Sample:	AOX, mg/kg Cl	
		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

**APPENDIX C RESULTS OF EXPERIMENTS FOR TESTING OF  
EFFECT OF VOLUME OF NITRATE STOCK  
SOLUTION**

Volume of nitrate stock, mL		8		12	
Sample	Unit	Batch 1	Batch 3	Batch 2	Batch 4
5 µg standard	µg Cl	4,64	4,78	4,85	4,86
SO-16R	mg/kg Cl	30,8	31,6	31,5	31,2
SO-7	mg/kg Cl	32,1	29,9	30,8	30,4
SOLID9A-146	mg/kg Cl	30,5	22,7	26,1	23,1
SO-8	mg/kg Cl	117	114	116	112
SO-9	mg/kg Cl	97,1	100	106	98
SO-4	mg/kg Cl	54,5	51,5	57,8	51,7
SO-1	mg/kg Cl	115	115	115	115
SO-13	mg/kg Cl	93,9	98,1	107	97,0
5 µg standard	µg Cl	5,01	5,02	5,10	4,85

**APPENDIX D RESULTS OF EXPERIMENTS FOR TESTING OF  
EFFECT OF COMBUSTION GAS FLOW**

Flow of combustion gas, mL/min		170	210	250
Sample	Unit			
5 µg standard	µg Cl	4,67	4,26	4,62
SO-4	mg/kg Cl	48,6	45,7	48,7
SO-4	mg/kg Cl	48,6	45,7	49,5
SL-4	mg/kg Cl	293	287	311
SL-4	mg/kg Cl	290	304	294
SO-4	mg/kg Cl	48,9	52,1	49,2
SL-4	mg/kg Cl	281	291	299
5 µg standard	µg Cl	4,40	4,34	4,73
SO-4	mg/kg Cl	51,3	44,8	52,2
SL-4	mg/kg Cl	288	300	299
5 µg standard	µg Cl	4,63	4,37	5,05

**APPENDIX E RESULTS OF EXPERIMENTS FOR TESTING OF  
EFFECT OF TEMPERATURE IN COMBUSTION  
CHAMBER**

Oven temperature, °C		1050	1000	950	900	850
Sample	Unit					
5 µg standard	µg Cl	4,85	4,81	4,75	4,53	4,19
SO-1	mg/kg Cl	115	114	112	118	97,7
SO-1	mg/kg Cl	116	113	111	115	101
SO-4	mg/kg Cl	51,4	50	50,6	51,2	46,3
SO-4	mg/kg Cl	53,8	52,3	46,4	48,9	49,1
SL-4	mg/kg Cl	296	293	304	288	256
SL-4	mg/kg Cl	314	305	285	304	328*
SL-4	mg/kg Cl	308	308	280	278	264
SL-4	mg/kg Cl	304	299	281	294	301*
SO-4	mg/kg Cl	53,3	49,9	49,1	48,4	45,4
SO-4	mg/kg Cl	49,7	50,9	48,8	48,1	47,3
SO-1	mg/kg Cl	111	116	107	116	115*
SO-1	mg/kg Cl	114	111	105	114	112
5 µg standard	µg Cl	5,08	5,16	4,6	5,02	4,97

\*: abnormal peak shape

**APPENDIX F RESULTS FROM COMPARISON OF WASHING PROCEDURES**

	Sample	AOX standard first draft		DIN standard	
		mg/kg Cl	mg/kg Cl	mg/kg Cl	mg/kg Cl
Soils	SO-1	110,3	111,2	121,4	121,5
	SO-4	50,3	49,3	51,4	46
	SO-7	30,9	28,1	33,6	33
	SO-8	111,3	111,7	118,9	121,5
	SO-9	88,2	93,7	93,3	100,2
	SO-13	134,5	114,9	119,3	118,6
	SO-16R	32,2	33,9	28,2	34,9
	SOLID-9 A	18,6	21,9	17,9	18,7
	SOLID-9 B	20,6	22,9	21,9	18,7
Sludges	SL-4	292	290	304,5	278,2
	SL-11	1784	1831	1944	2004
Composted waste	CW-1	521	528	513	530
	CW-5	90,6	89,5	108,5	106,5



**APPENDIX G RESULTS OF EXPERIMENTS FOR TESTING OF REPEATABILITY**

<b>Data from repeatability experiments</b>									
Sample	SO-1	SL-4	SO-1	SO-16R	SL-4	SO-16R	SO-7	1 µg std.	10 µg std.
Sub-sample weight, mg	10	10	50	50	50	100	100		
Measurement no.	Result, mg/kg Cl							Result, µg Cl	
1	56,58	271,88	91,5	25,85	296,17	33,03	34,94	0,99	10,94
2	72,12	241,56	95,53	25,92	301,56	32,82	29,67	1,04	11,08
3	66,62	219,2	98,58	23	296,23	32,73	29,75	1,03	11,03
4	42,29	236,98	93,91	19,09	303,3	33,17	30,65	0,97	11,01
5	64,91	245,9	96,12	18,88		32	29,78	0,98	
6	63,56	246,52	96,73	24,65		33,4	29,64	1,01	
7	64,58	262,06	97,26	22,11		33,37	29,22	1,1	
8	71,28	312,84	96,59	25,63		33,72	29,43	0,96	
9	66,3	264,62		22,2		34,08	30,15	1,01	
10	38,05	231,8		32,62		31,47	29,58	1	
11	60,18	230		18,11		31,88	29,83	0,98	
12	80,34	250,96		18,95		32,85	29,17	1,02	
Average	62,2	251,2	95,8	23,1	299,3	32,9	30,2	1,01	11,0
Standard deviation	12,0	24,7	2,19	4,19	3,67	0,77	1,56	0,038	0,058
Degrees of freedom	11	11	7	11	3	11	11	11	3
Amount of AOX per sample, µg	0,62	2,51	4,79	1,15	15,0	3,29	3,02	1,01	11,0

<b>Data from test of effect of combustion gas flow</b>								
Sample	SO-4	SL-4	5 µg standard					
Sub-sample weight, mg	100	25	Result		Std. dev.		Result Std. dev.	
Measurement no.	mg/kg Cl		mg/kg Cl		µg Cl		µg Cl	
Batch 1	1	48,6	293		4,67			
	2	48,6	290		4,40			
	3	48,9	281		4,63			
	4	51,3	288	5,10	0,146			
Batch 2	1	45,7	287		4,26			
	2	45,7	304		4,34			
	3	52,1	291		4,37			
	4	44,8	300	7,85	0,0569			
Batch 3	1	48,7	311		4,62			
	2	49,5	294		4,73			
	3	49,2	299		5,05			
	4	52,2	299	7,23	0,223			
Average		48,8	294,8		4,56			
Standard deviation		2,28	6,83		0,157			
Degrees of freedom		9	9		6			
Amount of AOX per sample, µg		4,88	7,37		4,56			