



### Challenge

Fast and trouble-free filtration of activated carbon / solid sample mixtures after the adsorption step of the shaking procedure in accordance with the requirements of EN 16166.

### Solution

Significant increase of the sample throughput by using the automatic filtration unit AFU 3.

## Determination of AOX in Sewage Sludge Samples by Batch Method According to EN 16166

### Introduction

Sewage sludge is a type of waste that is produced after wastewater treatment. It is composed of organic and mineral components, which are present in both dissolved and solid form. There are two basic types of sewage sludge: the raw sewage sludge and the treated sewage sludge, whereby the treatment serves the further utilization or disposal of the sewage sludge. Here procedures like anaerobic decomposition (in digestion towers), thickening, drainage, or drying are used. The forms of utilization for treated sewage sludge include its use as fertilizer, landfilling, and incineration, which can also be used to generate energy. Sewage sludge incineration (or co-incineration) represents the largest share of the individual types of recovery/disposal. All forms of recycling are subject to country-specific laws and regulations.

In addition to toxic heavy metals, such as chromium (VI), sewage sludge can contain a variety of organic pollutants that can be toxic, carcinogenic, or mutagenic. These substances include, among others, the substance classes of halogenated hydrocarbons (determined as sum parameters AOX – adsorbable organically bound halogens), PCBs (polychlorinated biphenyls), and PCDD/PCDFs (polychlorinated dibenzodioxins and dibenzofurans). Even if these substances are initially present in wastewater in low concentrations, they can be concentrated by processing the sewage sludge and reintroduced into the food chain by using it as fertilizer on arable land, for example. By setting limit values for certain elements (e.g., heavy metals) and organic compounds (e.g., AOX), sewage sludge and its recycling is well monitored by regulations in many countries. In the European

Union, the directive 86/278/EEC applies and in Germany, the so-called sewage sludge ordinance (AbfKlärV) ensures that both, humans and the environment are protected. AOX determination in sewage sludge is therefore one of the standard analytical procedures in environmental and agricultural laboratories as well as in laboratories of surveillance authorities.

EN 16166 describes a method for the determination of AOX in sludge, treated biowaste, soil, and sediments, which is widely used for the determination of AOX in sewage sludge. The AOX in this standard method is defined as the amount of chlorine, bromine, and iodine (not fluorine) present as organic compounds in the sample matrix and determined under the specified conditions. The result is expressed as chloride. The basic principle of the method is based on an enrichment step of the targeted analytes on activated carbon, followed by the combustion of the sample / activated carbon mixture in an oxygen stream at high temperatures. The hydrogen halides formed in this process are absorbed and determined e.g., by microcoulometry. The enrichment step of activated carbon is carried out by the shaking method. Here, activated carbon and the solid sample are brought into intensive contact, with the addition of a nitrate solution they are shaken for one hour in a glass vessel. This first sample preparation step can be very well automated with the help of so-called orbital shakers where many samples can be processed in parallel or "in a batch". The shaking is followed by the filtration of each individual sample in order to bring it into a feeding form suitable for the analyzer. Different filter materials can be used for the filtration step. In addition to commercially available membrane filters (here polycarbonate 0.45 µm), suitable other filter materials made of ceramic or quartz can also be used. During filtration, it is essential to avoid dry suction of the samples in order to reliably prevent contamination by the ambient air. This fact alone makes it clear that automation of the filtration step is difficult to achieve; the user must filter each individual sample in a controlled manner. Here, the use of the automatic filtration unit AFU 3 has proven well suited, which allows to filter three samples almost simultaneously but controlled by the user at any time.

## Materials and Methods

### Samples and Reagents

- Sewage sludge samples, dried and homogenized
- Standard solution p-chlorophenol containing 100 µg/L AOX
- Activated carbon, grain size approx. 10 to 50 µm
- NaNO<sub>3</sub> stock and washing solution
- 0.01 N HCl for the performance check of the AOX analyzer

### Sample Preparation

Three different sewage sludge samples were examined for their AOX content, two of which were samples from a German interlaboratory test. All samples were available in dried and homogenized condition. According to DIN 16166, 10 to 100 mg of the sample material were weighed into an Erlenmeyer flask with a nominal volume of 25 mL. Approximately 20 mg activated carbon and 10 mL nitrate stock solution were then added to each sample vessel. The prepared samples were then placed on a mechanical shaker (orbital shaker) and shaken intensively for one hour. Subsequently, the samples were filtered with the automatic filtration unit AFU 3. The sludge / activated carbon mixture was completely transferred into a quartz container filled with ceramic filter material. The filter cake was rinsed in portions with nitrate washing solution to completely remove inorganic chloride from the sample / carbon mixture. A total of 25 mL nitrate solution was used for each. The filtration was carried out by means of overpressure generated by an integrated powerful pump. All sample preparation steps were compliant to the procedure for the shaking method described in DIN EN 16166.

### Instrumentation

The three sewage sludge samples, each shaken with three different weights (approx. 10 mg, approx. 50 mg and approx. 100 mg), were available for analysis on the AOX analyzer multi X 2500 within a few minutes thanks to the simultaneous filtration with the AFU 3. The multi X 2500 was operated in vertical mode, the sample containers were automatically fed into the combustion system of the analyzer by means of the autoX 36 sampler. In order to achieve a quantitative conversion of all analytes, a so-called pre-combustion adapter was used for the incineration of the sewage sludge samples (which usually have a high organic load). This adapter allows the controlled drying and pre-digestion of the sample first at low temperature in the upper part of the vertical furnace. After a defined pre-combustion time (here two minutes) the sample is automatically transferred to the hot zone of the furnace. According to DIN EN 16166, a combustion temperature of 950 °C was set on the analyzer. Under these conditions the organically bound halogens are completely converted to hydrogen halides. These in turn are first transferred by the carrier gas to the drying section (concentrated sulfuric acid) and finally introduced into the coulometer cell. Here the halide ions are detected by argentometric titration. The result is given as chloride and represents the AOX content of the sample. It is not necessary to calibrate the analyzer because coulometric titration is one of the

absolute methods. To prove the functionality of the AOX instrument, control standards and blank values are measured every working day.

Table 1: Process parameters.

AOX analyzer multi X 2500	Specification
Combustion temperature	> 950 °C
Pre-combustion time	2 min
Titration delay	240 s
Maximum titration time	1200 s
Cell temperature	18–35 °C
Carrier gas	Oxygen 99.995% (4.5)
Working range coulometric cell "sensitive"	1 µg–100 µg Cl abs.
Extended working range	10 ng–1000 µg Cl abs.
Automation	autoX 36

## Results and Discussion

The three different sewage sludge samples were each analyzed three times, using three different weights. The results as well as the test of a commercial AOX standard are summarized in Table 2. A typical measurement curve is shown in Figure 1.

Table 2: AOX results of different sewage sludge samples.

Sample ID	Sample weight/ Volume	Amount inside the quartz container [µg] Cl abs.	Blank Value [µg] Cl abs.	Result AOX	Mean Value AOX ± Standard Deviation	RSD [%]
Sewage sludge 1 Interlaboratory test sample 75.2 mg/kg	13.2 mg	1.60	0.56	78.8 mg/kg	77.4 ± 1.2 mg/kg	1.6
	50.7 mg	4.44	0.56	76.5 mg/kg		
	98.3 mg	8.13	0.56	77.0 mg/kg		
Sewage sludge 2 Interlaboratory test sample 256 mg/kg	12.1 mg	3.72	0.56	261 mg/kg	258 ± 3.1 mg/kg	1.2
	51.6 mg	13.9	0.56	259 mg/kg		
	102.0 mg	26.6	0.56	255 mg/kg		
Sewage sludge 3	11.6 mg	5.18	0.56	398 mg/kg	404 ± 6.5 mg/kg	1.6
	48.6 mg	20.2	0.56	404 mg/kg		
	101.3 mg	42.2	0.56	411 mg/kg		
AOX standard 100 µg/L	100 mL	10.47	0.56	99.1 µg/L	-	-

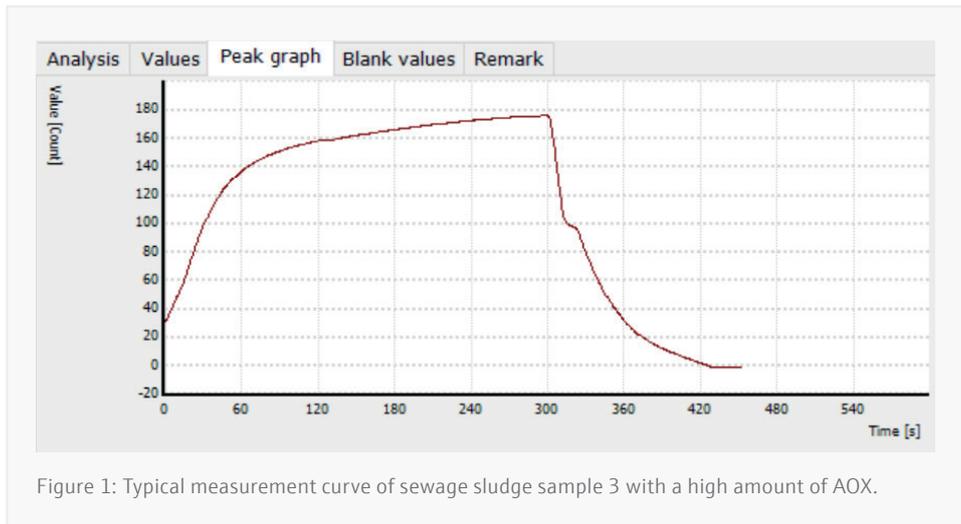


Figure 1: Typical measurement curve of sewage sludge sample 3 with a high amount of AOX.

The different weights delivered comparable results with a relative standard deviation of well below 2%, which underlines the excellent handling of the shaking method by means of AFU 3. The main advantage in handling with the AFU 3 is that the mixture of sample and activated carbon is transferred directly into a quartz container. If the filtration is carried out via a conventional vacuum filtration apparatus on a membrane filter, e.g., made of polycarbonate, there is the danger of dry suction, because very moist membrane filters can only be transferred without loss into a sample boat for the AOX analyzer with difficulty. As a result, the risk of contamination of the sample by ambient air is significantly higher. The overpressure filtration at the AFU 3 additionally minimizes the contamination risk by the possibility of an inert gas connection. The filtration of up to three samples can run almost simultaneously, so that the filtering of the samples is no longer the speed-determining step of the sample preparation.

The shape of the measurement curve clearly shows that the combustion process using the pre-combustion adapter and the introduction of HX into the coulometric measuring cell is very controlled and fast (rapid rise and reaching a signal plateau after a short time). The subsequent titration (descending signal curve) is carried out with adapted, dynamic titration currents, so that over-titration and thus false high AOX values are reliably prevented. Even with high contents, the titration progress is fast and the special cell electrolyte ensures that even unexpectedly high AOX loads or long sample series can be measured reliably and without interference.



Figure 2: multi X 2500 vertical with autoX 36



Figure 3: AFU 3

## Conclusion

The measurement results prove that correct and precise results for the AOX content in sewage sludge samples according to DIN EN 16166 can be achieved with the aid of the automatic filtration unit AFU 3 and the multi X 2500. The risks of using the conventional shaking method with membrane filters (e.g., loss of AOX during transfer or contamination by ambient air during dry suction) are significantly minimized by using the AFU 3. Furthermore, the sample throughput can be increased by the simultaneous filtration of three samples. This makes the AFU 3 an ideal tool even for inexperienced laboratory personnel.

## References:

EN 16166:2012- "Sludge, treated biowaste, soil and sediments – Determination of adsorbed organically bound halogens (AOX)"

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