



Challenge

Complete adsorption on activated carbon by batch method for AOX determination in complex aqueous sample matrices with high particle load

Solution

Fast filtration of challenging wastewater samples with the semi-automatic AOX sample preparation system AFU 3

Intended audience

Industrial wastewater treatment plants, municipal waterworks, authorities for environmental protection, contract laboratories, industrial wastewater labs

Determination of AOX in Wastewater Samples by Batch Method in Accordance with EN ISO 9562

Introduction

The parameter AOX (adsorbable organically bound halogens) is mainly used for monitoring water quality. In many countries, it also plays an important role in the evaluation of sewage sludge and solid waste and their aqueous eluates.

The determination of this parameter is of interest to municipal wastewater treatment plants, monitoring authorities, and industrial companies (direct and indirect dischargers of wastewater). In many places, industrial dischargers are required to verify that the wastewater they discharge to the environment or to a public wastewater treatment facility does not exceed the industry specific AOX limit. Wastewater treatment plants must monitor not only compliance with the limits, but also the effectiveness of their treatment process by comparing AOX levels before (influent) and after (effluent) treatment. Finally, state authorities ensure that the pollution of surface waters with organically bound halogens (AOX) is kept as low as possible.

The determination of AOX is an analytical convention that covers the sum of organically bound chlorine, bromine, and iodine, but not fluorine, which can be adsorbed on activated carbon under exactly defined conditions. For unfiltered water samples, the result also includes the AOX content adsorbed on suspended matter. The AOX parameter is used worldwide, a frequently applied method for this purpose is ISO 9562. This norm describes three adsorption methods with activated carbon for AOX determination: the stirring, the shaking (or batch), and the column method. The choice of adsorption process is partly determined by legal or by internal laboratory requirements.

The carbodisc or stirring method requires very experienced laboratory personnel and a high manual effort. For these reasons it is rarely used in routine laboratories. In addition, it is not well suited for water samples containing particles, as it is the case with most wastewater samples.

The column method enables adsorption of both, particle-free and particle-containing samples. It offers many advantages to the user, especially for challenging wastewater samples. Besides a simple possibility to control the completeness of the AOX adsorption on the activated carbon, it is more "robust" for samples with high chloride concentrations (up to 1 mg/L Cl⁻), because a more effective rinsing of the adsorption columns with nitrate washing solution is possible. Furthermore, the column method is characterized by a high degree of automation and thus offers a high sample throughput with minimal maintenance. The risks of contamination and handling errors are reduced by using pre-filled activated carbon columns, which also minimizes interaction with the laboratory atmosphere. If samples containing particles are to be adsorbed, it is possible to connect a filter column upstream of the activated carbon columns. This has the advantage that the particles contained are collected and thus clogging of the activated charcoal columns is effectively prevented.

The use of the batch or shaking method is mandatory for sewage sludge and other solid samples, but is often used

for water samples, too. According to ISO 9562, the batch method should not be used for water samples in which the (inorganic) chloride concentration cannot be reduced by dilution to a value ≤ 500 mg/L Cl⁻. The degree of automation for shaking is arbitrarily high; depending on the available circular shaker, many samples can be enriched on activated carbon in parallel.

The subsequent filtration step can only be automated to a limited extent. Typically, commercial systems can filter up to three samples simultaneously. Membrane filters made of polycarbonate with a pore size of 0.45 μm are frequently used as filter material (according to ISO 9562), other materials such as ceramic wool are suitable as well. The tendentially higher risk of contamination of samples when using the batch method can be significantly minimized by using a suitable filtration apparatus in which the contact time of the enriched carbon with the laboratory atmosphere is limited. A suitable combination of filter material and apparatus allows wastewater samples with high particle loads to be filtered off quickly and completely.

Materials and Methods

Sample preparation was carried out according to the batch method using the AFU 3 automatic filtration unit. The determination of AOX was carried out with the multi X 2500. The analyzer was operated with a vertically arranged combustion tube made of quartz glass. Samples enriched on activated carbon columns were automatically fed to combustion using the autoX 36 autosampler. The detection of the formed hydrogen halides was carried out by coulometric titration.

Samples and reagents

- Five wastewater samples of different origin
- Control standard solution, 4-chlorophenol in water, c: 100 $\mu\text{g/L}$ AOX
- Activated carbon for AOX determination in accordance with batch method
- Concentrated nitric acid (HNO₃), 65%, to acidify samples
- Concentrated sulfuric acid (H₂SO₄), 96%, for drying of reaction gases at the AOX analyzer
- Sodium nitrate stock and wash solution (NaNO₃) in accordance with ISO 9562
- Hydrochloric acid (HCl), c: 0.01 mol/L, for functionality check of the AOX analyzer

Sample preparation

Five different wastewater samples were analyzed for AOX, each in two different dilutions. Two samples contained wastewater (influent and effluent of a water treatment plant) from a laundry for workwear and cleaning cloths, two other samples came from the textile industry (also influent and effluent). In addition, one wastewater sample from an interlaboratory test was examined.

All wastewater samples examined had already been acidified with concentrated HNO₃ to a pH ≤ 2 after sampling and were stored in a refrigerator at approx. 4 °C until they were measured. To determine the AOX content, the samples were first warmed to room temperature, diluted, and again adjusted to a pH ≤ 2 using concentrated nitric acid. Subsequently, 100 mL of each sample was filled into Erlenmeyer flasks and 5 mL of nitrate stock solution was added according to ISO 9562. After the addition of 50 mg activated carbon, the Erlenmeyer flasks were sealed with a ground-glass stopper, placed on a circular shaker, and shaken for one hour. This enrichment procedure was followed by a filtration and washing procedure. For this purpose, the batch samples including the activated carbon were transferred into the filtration vessels of the AFU 3 and filtered with the aid of overpressure into the quartz containers filled with filter material below. The activated carbon retained in the quartz containers was then rinsed with approx. 25 mL of the nitrate wash solution in accordance with ISO 9562.

Calibration

Since the coulometry used to detect the AOX is an absolute detection method, calibration of the AOX analyzer was not necessary. To check its functionality, the coulometric measuring cell was tested with 0.01 mol/L HCl. For this purpose, 50 µL of this hydrochloric acid was injected directly into the coulometer cell (cell test) using a microliter syringe. In doing so, $17.73 \mu\text{g} \pm 0.53 \mu\text{g}$ chloride should be detected by the system. Another way to check the AOX analyzer is to combust 0.01 mol/L HCl (furnace test). For this purpose, 50 µL of the hydrochloric acid is dosed into a quartz tube filled with ceramic wool and transferred to the analyzer's furnace. The recovery for chloride should be within the same limits as for direct injection of HCl into the measuring cell. In addition, AOX analysis includes a daily check of the overall procedure. For this purpose, AOX control standards are first adsorbed on activated carbon and then burned and detected in the analyzer. In accordance with ISO 9562, the measured value of the control standard should not deviate by more than 10% from the theoretical value, which means a recovery rate of between 90% and 110%.

Instrument settings and method parameters

The AOX determination was carried out with an AOX analyzer type multi X 2500 in vertical operating mode. Samples were fed to the combustion tube using the autoX 36 autosampler. A volume of 100 mL of each of the previously diluted samples was used for enrichment on activated carbon. The quartz containers filled with filter material and loaded activated carbon were placed in the tray of the autoX 36 after filtration. The sample feeding of the quartz containers into the vertically arranged open combustion tube was fully automatic. The furnace temperature of 950 °C was selected in accordance with ISO 9562. During combustion, the organic halogen compounds adsorbed on the activated carbon are converted to gaseous hydrogen halides (HX, HCl). After drying the combustion gases with the aid of concentrated sulfuric acid, the HCl gas is transferred to the coulometer cell. This cell has a wide operating range from 1 µg to 100 µg chloride absolute, and chloride detection is performed by argentometric titration. Parallel to the sample preparation, which included a one-hour enrichment of the analytes on activated carbon by intensive shaking on the circular shaker, the analyzer was put into operation. Proper operation was verified using a cell or furnace test. Prior to the determination of AOX in the wastewater samples, blank determinations and measurements with control standards were performed.

Table 1: Method parameter multi X 2500

Parameter	Setting
Furnace temperature	950 °C
Titration delay	12 (= 360 s)
Maximum titration time	600 s
Cell temperature	21 °C
Sample supply	autoX 36

Results and Discussion

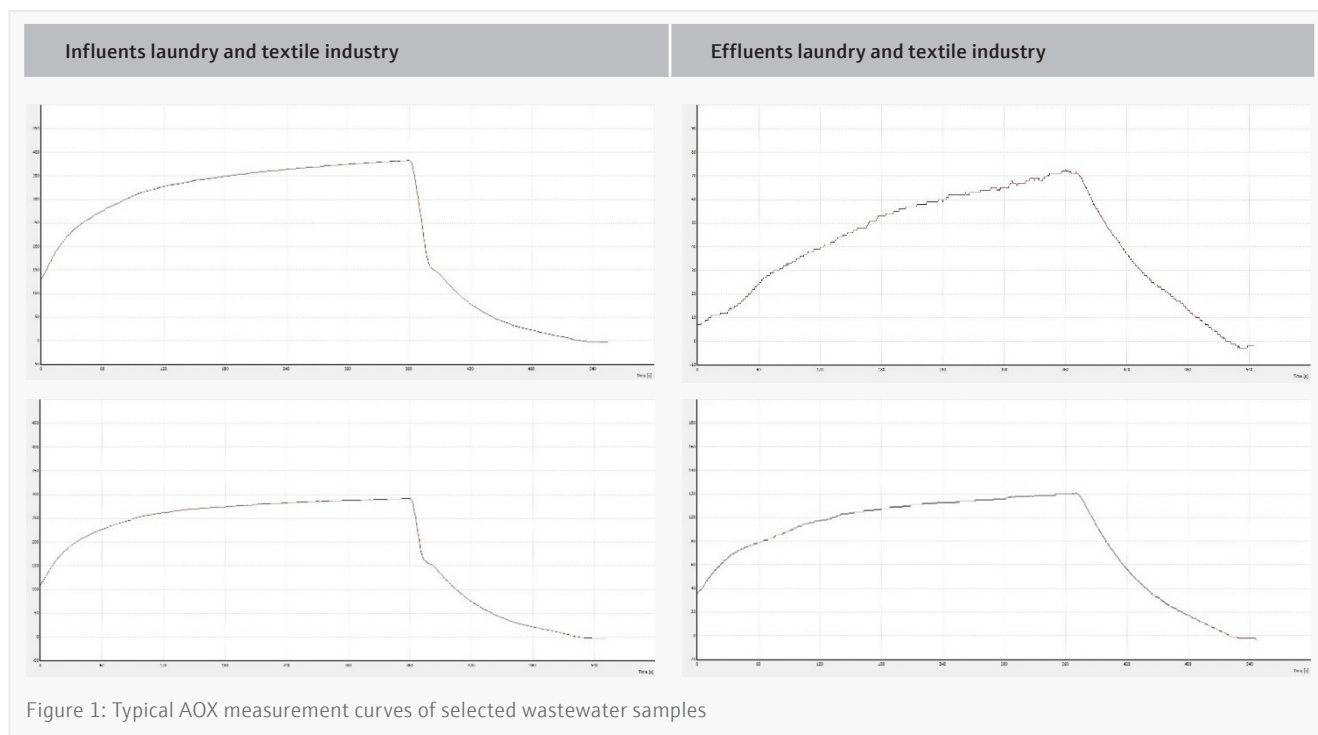
The analytical results of all tested wastewater samples and control standards are summarized in Table 2. The measurements for the samples were each performed as a duplicate determination for two different dilutions. The blank value determined prior to these measurements from a triple determination was 0.38 µg Cl absolute on average. It was automatically taken into account in all subsequent sample measurements by the multiWin software. The AOX standard was measured undiluted.

Table 2: Blank-corrected results of AOX determination of wastewater samples and standards

Sample ID	Determination	Dilution	AOX value [$\mu\text{g/L}$]	Mean value AOX [$\mu\text{g/L}$]
Control standard c: 100 $\mu\text{g/L}$ AOX	1	-	97	99
	2	-	101	
Influent Laundry	1	1 in 20	1820	1860
	2	1 in 50	1900	
Effluent Laundry	1	1 in 5	235	244
	2	1 in 10	253	
Influent Textile industry	1	1 in 10	423	437
	2	1 in 20	451	
Effluent Textile industry	1	1 in 2	73	75
	2	1 in 5	77	
Wastewater round robin test 583 $\mu\text{g/L}$ AOX	1	1 in 10	559	572
	2	1 in 20	585	

According to ISO 9562, the results for two different dilutions of one and the same sample should not differ by more than 10%. The obtained results meet this requirement and thus demonstrate the general suitability of the batch method as a sample preparation procedure and of the AOX analyzer as a precise measuring instrument.

Typical measurement curves for the determinations of the effluents and influents of laundry and textile industry are shown as examples in Figure 1.



Summary

The measurements carried out show that sample preparation using the batch method by means of AFU 3 provides reliable AOX results for various types of challenging wastewater samples. Even samples with complex matrices or higher particle load can be prepared and analyzed quickly and reliably after appropriate dilution and enrichment on activated carbon. With the automatic filtration unit AFU 3, up to three samples can be transferred simultaneously into quartz containers. The multi X 2500 AOX analyzer features robust detection and simple automation and is ideally suited for AOX determination in wastewater samples.



Figure 2: AFU 3 sample preparation unit



Figure 3: multi X 2500 – AOX analyzer

Recommended device configuration

Table 3: Overview of devices, accessories, and consumables

Article	Article number	Description
multi X 2500	450-126.430	AOX/TOX, EOX, POX analyzer
multiWin software	450-011.803	Control and data evaluation software
autoX 36	450-126.412	Autosampler for 36 samples
AFU 3	450-126.971	Automatic Filtration Unit
Kit "batch method" for AFU 3	450-126.972	Accessory for batch method for AFU 3

References

[1] ISO 9562:2004 "Water quality - Determination of adsorbable organically bound halogens (AOX)"

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