Application Note · multi X 2500

Challenge

Quick and reliable adsorption on activated carbon using column method to save time for sample preparation.

Solution

With the APU sample preparation units series even challenging wastewater samples can be adsorbed very fast onto activated carbon columns, fully compliant with the relevant international AOX regulations.

Determination of AOX in Wastewater Samples by Column Method According to DIN EN ISO 9562

Introduction

The parameter AOX (adsorbable organically bound halogens) is mainly used for monitoring water quality, but it also plays an important role in the evaluation of solid waste (e.g., in aqueous waste eluates) and sewage sludge. It is of interest for municipal sewage treatment plants, environmental surveillance authorities, but also for industrial companies, which directly and indirectly discharge their wastewaters. Industrial dischargers are obliged to check that the wastewater they discharge into the environment resp. into a public sewage treatment plant does not exceed the industry-specific AOX limit value. Sewage treatment plants must not only monitor compliance with the limit values but also the effectiveness of their treatment process by comparing the AOX content before and after treatment. Finally, state authorities ensure that the pollution of surface waters with organically bound halogens is kept as low as possible.

The determination of AOX is an analytical convention that describes the sum of organically bound chlorine, bromine, and iodine (but not fluorine), which can be adsorbed on activated carbon under precisely defined conditions. In case of unfiltered water samples, also AOX contents adsorbed on suspended solids are included in the result. The parameter is used internationally and therefore standardized, e.g., according to ISO 9562, which is applied in many countries. The ISO 9562 describes three adsorption procedures with activated carbon for AOX determination: the stirring, the shaking and the column method. The choice of the adsorption method is determined by laboratory or administrative regulations. In many countries the determination of AOX in wastewater samples using the column method is mandatory.

The *stirring method*, also called carbodisc method, requires very experienced lab personnel and high manual effort. For these reasons it is rarely used in routine labs. Furthermore, it is not very suitable for water samples containing particles, like typical wastewater samples do. The shaking or *batch method*, for example, is mandatory for sewage sludge and other solid samples, but also often applied to water samples. However, the major disadvantages of this method are its limited degree of automation, a higher risk of contamination from the lab environment, and last, but not least, a missing simple control possibility regarding the completeness of the AOX adsorption step. The batch method is not recommended to be used for water samples where (inorganic) chloride concentration cannot be reduced to a value ≤ 500 mg/L Cl^- by dilution.
The *column method* enables the adsorption not only of particle-free, but also of particle-containing samples and offers a lot of advantages for the user especially for challenging wastewater samples. Besides a simple possibility to control the completeness of the AOX adsorption step, it is more robust for samples with high chloride concentrations (up to 1 mg/l Cl^-), because of a more effective charcoal rinse procedure by the nitrate washing solution. Furthermore, it allows for a high degree of automation, which results in a high sample throughput and minimal maintenance effort. The risks of contamination and handling errors are reduced by using prefilled AOX columns for adsorption, which minimizes interaction with the lab atmosphere. For particle-containing samples there is the possibility of fitting a filter column upstream of the columns filled with activated carbon. This ensures that the particles are separated and thus also prevents the activated carbon columns from potentially becoming clogged.

Materials and Methods

Samples and Reagents

- Wastewater samples of different origin
- Standard solution p-chlorophenol containing 100 µg/L AOX
- Prefilled columns with 50 mg activated carbon
- Concentrated HNO_3
- $NaNO_3$ stock and washing solution
- 0.01 N HCl for performance check of the AOX analyzer

Sample Preparation

Three different water samples were analyzed, each in two different dilutions. One sample was obtained from an industrial water treatment plant (effluent) with a DOC (dissolved organic carbon) content of approx. 50 mg/L. Another sample with a high particle load and a high DOC content (about 1 g/L) was a raw sewage from a chemical plant. This wastewater with a complex matrix contained approx. 10 g/L of inorganic chloride. The third wastewater was a sample from a German round robin test, containing a small particle load. All samples were diluted in two different ratios to demonstrate the advantages of the column method when samples with difficult matrices (high particle load, high content of chloride, high amount of DOC) are adsorbed. According to DIN EN ISO 9562 results for two different dilutions of one and the same sample should not differ by more than 10%.
The wastewater sample with high particle load was homogenized prior to adsorption by using a high-speed stirrer (disperser). After dilution all samples were adjusted to a pH value of 2 with concentrated nitric acid. Finally, 5 mL of nitrate stock solution was added to 100 mL of each diluted and acidified sample. Prepared samples were filled into syringes and placed onto the APU sim sample preparation unit. Adsorption was carried out automatically by passing the samples through the activated carbon columns (filled with approx. 50 mg activated carbon each) at a flow rate of 3 mL/min, followed by automatic rinsing with nitrate washing solution at the same flow rate. All sample preparation steps were compliant to the procedure for column method as regulated by the DIN EN ISO 9562.

Table 1: Column method settings

Sample preparation: APU sim	Settings
Sample volume	100 mL
Nitrate washing solution	25 mL
Flow rate	3 mL/min

Instrumentation

Sample preparation with the APU sim sample preparation unit was completed within approximately 45 minutes for all six diluted samples due to its simultaneous operation mode. The final AOX determination was carried out using the multi X 2500 AOX analyzer in vertical operation mode. For the automated sample supply the autoX 36 sampler was used. The prepared AOX columns were placed into the tray of the autoX 36. This sampling system automatically introduces the loaded columns into the vertically arranged open AOX combustion tube. The furnace temperature of 950 °C was chosen in compliance with DIN EN ISO 9562. During combustion the organic halogen compounds were converted to HCl gas. After drying with concentrated sulfuric acid, the HCl gas was transferred into the micro coulometric measuring cell. The cell has a wide working range from 1 µg to 100 µg chlorine absolute. The chlorine detection was carried out by means of argentometric titration. Proper operation of the analysis system was confirmed by analysis of a commercial AOX standard solution (4-chlorophenol in water). As micro coulometric chlorine determination is an absolute method, no calibration of the analyzer is needed.

Table 2: Process and detection parameter settings

multi X 2500	Specification
Furnace temperature	> 950 °C
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.
Entire working range	10 ng–1000 µg Cl abs.
Sample supply	autoX 36 resp. autoX 112

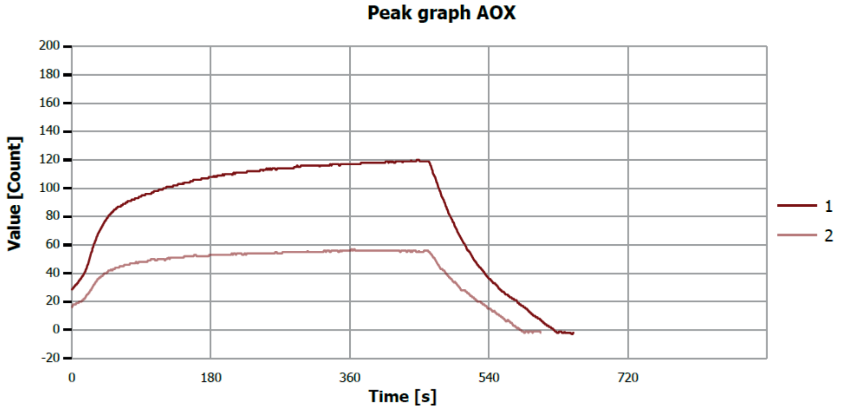
Results and Discussion

The three different wastewater samples were each analyzed twice in two different dilutions. The results and the measurements of a commercial AOX standard are summarized in table 3. Typical measuring curves are shown in table 4. The different dilution ratios deliver comparable results with deviations far less than 10%, thus demonstrating the general suitability of the column method for each single wastewater sample.

Table 3: AOX results of different water samples in different dilutions

Sample Name	Adsorption Volume [mL]	Dilution ratio	Column 1 [µg] Cl abs.	Column 2 [µg] Cl abs.	Blank Value [µg] Cl abs.	Result AOX [µg/L]
Effluent	100	1 in 2	4.91	0.63	0.30	104.8
	100	1 in 5	2.10	0.41	0.30	110.5
Industrial wastewater	100	1 in 10	9.05	4.22	0.30	1297
	100	1 in 50	2.42	0.54	0.30	1330
Wastewater round robin test, 583.3 µg/L		1in 5	11.68	0.20	0.30	579
		1 in 10	6.03	0.11	0.30	584
AOX standard 100 µg/L	100	none	10.40	0.23	0.30	103.3

Table 4: Example of a measuring curve

Sample Name	Measuring curve showing column 1 and column 2
Industrial wastewater, dilution ratio 1 in 10 Column 1 (9.05 µg Cl abs.) Column 2 (4.22 µg Cl abs.)	

The curves illustrate quite clearly the analytical advantage of the column method compared with the batch method. Both curves represent an absolute amount of AOX (expressed as Cl), which has been adsorbed on the surface of the activated carbon. The quality of the adsorption can be assessed through the ratio of the absolute contents to each other. As a general rule, the first column contains several times more AOX than the second column, which means that the first curve is “higher” than the second one. This is called a complete adsorption. Ideally, the absolute content of the second column is in the blank value range of the activated carbon. Depending on the type of the water sample, specific matrix components might interfere with the adsorption process. In such a case, the absolute amounts of Cl of the individual columns can be equal or the second column can be even higher than the first. This is called a „breakthrough“ of the AOX on the activated carbon.
The example curves of the industrial wastewater sample are showing the influence of the complex matrix of this sample: column 2 contains nearly 50% of the content of column 1, so a „breakthrough“ can be assumed. A second analysis with the same sample but in a higher dilution ratio helps to verify whether the adsorption process was complete or if an AOX “breakthrough“ has occurred. The result of the 1 in 50 diluted sample (1330 µg/L AOX), where only approx. 20% of column 1‘s content can be found on column 2, is nearly the same as for the less diluted sample (1297 µg/L AOX). This finally confirms that no AOX “breakthrough“ took place during the sample adsorption step. Experienced users can easily judge the quality of AOX results by evaluating the curves of the two columns. Often there is no need for a repeated analysis of the same sample in a higher dilution ratio. When applying the batch method to such a sample, no statements can be made about the completeness of the adsorption step, since only one aliquot of activated carbon is used for AOX adsorption and measurement by the batch method. Therefore, it is a must to run replicates with different dilution ratios to avoid falsified results.

Figure 1: APU sim

Figure 2: APU 28

Conclusion

The provided measurement results show that sample preparation by column method provides reproducible AOX results for different types of challenging wastewater samples. Even samples with high particle loads and complex matrices (high salt and DOC levels) could be adsorbed onto activated carbon quickly and reliably. The APU sim sample preparation unit enables to process six samples simultaneously in less than one hour without manual intervention. Compared to the time and labor-intensive batch method, the AOX analysis according to the column method is faster and cost-effective.
For larger sample series or higher throughput demand, the versatile systems of the APU 28 series are recommended. They enable automatic AOX sample preparation according to the column method for up to 28 samples. The sequential mode of operation, with overnight adsorption of the samples by APU 28 and subsequent analysis of the enriched AOX columns with the multi X 2500 during the day, is not only extremely time-saving, but also guarantees a high sample throughput around the clock.

References

1) DIN EN ISO 9562:2004 "Water quality—Determination of adsorbable organically bound halogens (AOX)"

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