Application Note AN-CIC-034

通燃子色法(CIC)快速分析水中的可吸附有机素(AOX)

Measurement of AOCl, AOBr, AOI, and AOF according to DIN 38409-59 and ISO/DIS 18127

SUMMARY

AOX (adsorbable organically bound halogens) is a complex parameter covering the sum of halogenated organic compounds adsorbable on activated carbon. Many of these organohalogens and their degradation products pose serious risks to human health and the environment [1–4]. Monitoring them is essential to ensure appropriate water quality, to trace their sources, or to investigate the efficiency of AOX removal techniques in water treatment processes. Historically, AOX was determined via microcoulometric titration after adsorption of water samples on activated carbon and subsequent combustion (DIN EN ISO 9562 or EPA 1650) [1,2]. By definition, based on the technical setup, AOX was comprised of adsorbable organically bound chlorine (AOCl), bromine (AOBr), and iodine (AOI)—but not fluorine (AOF)—as a sum parameter and not its individual fractions. Both **DIN 38409-59** and **ISO/DIS 18127** describe a validated procedure of adsorption and analysis via **combustion ion chromatography (CIC)** to determine **AOCl**, **AOBr**, **AOI**, **AOF**, and the sum parameter **CIC – $AOX_{(Cl)}$**. This Application Note explains the CIC method used to fulfill the requirements of these standards for AOCl, AOBr, AOI, AOF, and AOX analysis.

EXPERIMENTAL

This application is focused on the experimental approach of AOX analysis. More detailed information can be found in related Metrohm literature (WP-081, AN-CIC-033 – specifically about AOF). The complete validation dataset of DIN 38409-59 is available on the Water Chemistry Society webpage.

The overall sample preparation procedure, i.e., preconcentration and adsorption of organically bound halogens, resembles that of DIN EN ISO 9562, as adsorption on activated carbon is a key point for both methods (**Figure 1**). While for AOF it is crucial that the samples are neutral to avoid adsorption of inorganic fluorine to the activated carbon, sample acidification is mandatory for the other organically bound halogens, similar to DIN EN ISO 9562. For CIC-$AOX_{(Cl)}$ determination (i.e., AOCl, AOBr, and AOI), samples need to be acidified with nitric acid to pH <2 prior to preconcentration (**Table 1**).

The adsorption of the organically bound halogens is handled in a semi-automated manner using the APU sim system from Analytik Jena (**Figure 1**). Two columns filled with activated carbon (at least 50 mg in each column) are connected in series and 100 mL of sample is passed through. The organically bound halogens adsorb to the activated carbon (using dedicated disposable columns for AOF and AOX determination, **Table 1**), while inorganic halogens are rinsed off (**Figure 1**).

After the semi-automated sample preparation is

finished, the complete content of the two adsorption columns is transferred into one or two separate ceramic boats for CIC analysis. Combustion occurs at temperatures above 950 °C in the presence of argon and oxygen (**Figure 1**). For pyrohydrolytic combustion, a water stream is essential as it converts the halogens into their hydrogenous forms. Chlorine, bromine, iodine, and fluorine are volatilized in the combustion step, transported into the absorber solution (ultrapure water) with an argon/oxygen gas stream, and transferred into the liquid phase (**Figure 1**). Dosinos guarantee precise automated liquid handling, e.g., the transfer of the aqueous sample into the IC for analysis, or the water stream essential for pyrohydrolytic combustion.

The ion chromatographic separation is achieved on a Metrosep A Supp 5 - 250/4.0 column in combination with the A Supp 5 Guard/4.0. AOF (as F) elutes in under 7 minutes while AOX (i.e., Br, Cl, and I) elutes in less than 25 minutes (**Figure 2**). Automatic system calibration with MiPT (Metrohm intelligent Partial-Loop Injection Technique) is performed using inorganic anion standards for fluoride, chloride, bromide, and iodide (1 g/L standard solutions, TraceCert® from Sigma-Aldrich).

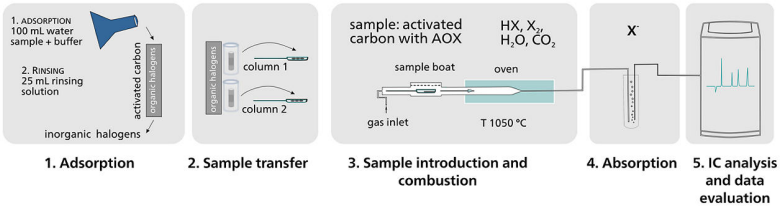

Figure 1. Schematic of the procedure for AOX (WP-081) and AOF (AN-CIC-033) analysis. The first step is adsorption performed with the APU sim (Analytik Jena) for semi-automated and standardized adsorption of up to six samples in parallel. After the second step of sample transfer into the combustion boats, the sample is automatically combusted (step 3, combustion module from Analytik Jena consisting of a combustion oven with Auto Boat Drive (ABD) and an autosampler (MMS 5000)). In the fourth step, the volatilized halogens are transported to the absorber solution via gas stream (920 Absorber Module). The last step (5) is the automatic analysis of AOBr, AOCl, and AOI, or of AOF with the IC (930 Compact IC Flex) including data evaluation. The complete CIC process is fully automated and controlled by MagIC Net software from Metrohm.

Table 1. Parameters for AOF and AOX (AOCl, AOBr, and AOI) sample preparation.

	AOF	AOCl, AOBr, AOI
pH	Neutralized	Acidified to pH <2 with nitric acid
Buffer	0.5 mL 2 mol/L sodium nitrate	0.5 mL 2 mol/L sodium nitrate, acidified with nitric acid
Sample volume	100 mL	
Rinsing solution	25 mL	
	0.01 mol/L sodium nitrate	0.01 mol/L sodium nitrate, acidified with nitric acid
Absorption columns	Two activated carbon tubes (disposable, from Analytik Jena)	
	402-880.616	402-880.610
Flow rate APU sim	3 mL/min	

Performance checks of AOF and AOX determinations and the standard series for LOD determination (**Table 2**) are accomplished using organic reference standard solutions with varying concentrations (4-fluorobenzoic acid, 4-chlorobenzoic acid, 4-bromobenzoic acid, and 4-iodobenzoic acid), treated in the same way as the samples.

As the procedure for the determination of AOX is rather complex, dedicated sample boats and charcoal (i.e., fluoride-free materials for AOF, **Table 1**) and blank measurements are essential to guarantee a low background and an appropriate blank correction (**Equation 1**).

RESULTS

Individual concentrations for AOCl, AOBr, AOI, and AOF are calculated according to **Equation 1**. A sum parameter for AOX (CIC-$AOX_{(Cl)}$) is calculated using **Equation 2**. However, due to the novelty of this validated approach, CIC-$AOX_{(Cl)}$ has not yet replaced AOX in water or wastewater regulations.

Dedicated materials and the sensitive analysis of the halogens with suppressed conductivity detection results in low blank values. Blank values were only measurable for fluoride and chloride (**Table 2**). The requirements for DIN 38409-59 are fulfilled—in fact, the overall procedure here is even more sensitive.

$$c(X_{ads}) = \left(c(X^-)_{IC} * \frac{V_{Abs}}{V_{Smpl}}\right) - \left(c(X^-_{BW})_{IC} * \frac{V_{AbsBW}}{V_{SmplBW}}\right)$$

Equation 1.

$c(X_{ads})$	Mass concentration of individual adsorbable organically bound halogens (with X = Cl, Br, I, and F) in µg/L
$c(X^-)$	Halogen concentration in the sample's absorption solution in µg/L (with X = Cl, Br, I, and F) in µg/L
V_{Abs}	Final volume of the absorption solution in L
V_{Smpl}	Volume of the sample that was used for adsorption; always 0.1 L
$c(X^-)_{BW}$	Halogen concentration in the absorption solution of the blank in µg/L
V_{AbsBW}	Final volume of the absorption solution of the blank in L
V_{SmplBW}	Volume of the blank solution that was used for adsorption; always 0.1 L

$$c(CIC\text{-}AOX_{(Cl)}) = c(AOCl) + c(AOBr) \cdot 0.4437 + c(AOI) \cdot 0.2794$$

Equation 2.

$c(CIC\text{-}AOX_{(Cl)})$	Sum concentration of adsorbable organically bound halogens in µg/L as mass concentration based on chloride

During the DIN validation process, several water samples were analyzed from different laboratories using similar setups (validation report: wasserchemische-gesellschaft.de).

Table 2. Blank, LOD (limit of detection), and DIN scope for the determination of adsorbable organically bound halogens. LODs are determined according to DIN 32645. For AOBr and AOI, the LODs are determined using the calibration curve as no blank values were found. For AOF and AOCl, the blank method was applied (DIN 32645).

	Blank (µg/L)	LOD (DIN 32645) (µg/L)	Scope of DIN application (µg/L)
AOF	1.1	0.38	2
AOCl	2.6	1.36	10
AOBr	0	0.24	1
AOI	0	0.47	1

Using IC, it is now possible to not only determine the sum parameter CIC-AOX$_{(Cl)}$, but also to measure the individual fractions contributing to the AOX contents (**Figure 2**, WP-081) and to assess AOF (AN-CIC-033).

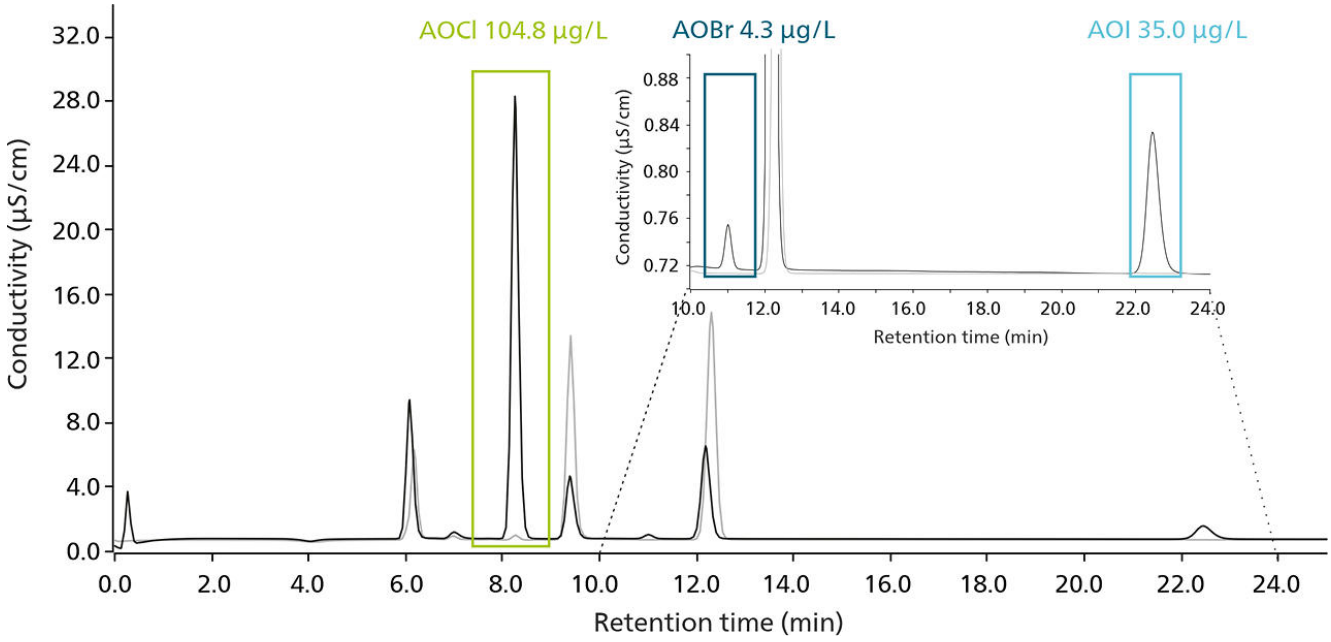

Figure 2. Chromatogram overlay of the blank and a wastewater sample for the determination of AOCl, AOBr, and AOI measured from absorption column #1. To calculate the mass concentration of the individual AOX fractions, blank correction was performed according to Equation 1. No halogens were adsorbed on column #2, revealing the retention efficiency for AOX on column #1.

CONCLUSION

Overall, the validated procedure benefits from its easy, straightforward, and standardized handling, the precise determination of the analytes, the automatic calculation of results, and a low-maintenance, single-manufacturer setup.

A significant advantage of the standards DIN 38409-59 and ISO/DIS 18127 is that they allow the determination of adsorbable organically bound halogens as individual sum parameters, i.e., AOCl, AOBr, AOI, as well as AOF (a screening parameter for «total» PFASs, AN-CIC-033). Automation (e.g., automated eluent production, MiPT, intelligent and logical MagIC Net features) improves repeatability, accuracy, and reliability of the results, saves valuable laboratory time for the liquid handling, standard, and eluent preparation, and allows 24/7 analysis – from which every laboratory, either research, routine, or governmental lab – can profit.

The world of organically bound halogens is so varied that these sum parameters enable insights about hot spots, transport pathways, but also particularly vulnerable regions in a very simple way, while complex targeted analysis, if at all, can resolve individual organically bound halogens for deeper investigations afterwards.

REFERENCES

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4. Xie, Y.; Chen, L.; Liu, R. AOX Contamination Status and Genotoxicity of AOX-Bearing Pharmaceutical Wastewater. *J Environ Sci* **2017**, *52*, 170–177.

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CONFIGURATION

Metrosep A Supp 5 - 250/4.0

瑞士万通的分柱以其高分度可用于度大的分任。即便是的分也可用 Metrosep A Supp 5 - 250/4.0 松解决,且其解决方法可重。柱的高容量可在不行品前理的情况下定 150 mg/L 化物中的 1 µg/L 酸。此柱的使用范不止用来定准子。在半体工中或厂的炉水程中控制高准的度要求,Metrosep A Supp 5 - 250/4.0 柱是宜的。

Metrosep A Supp 5 Guard/4.0

Metrosep A Supp 5 Guard/4.0 IC 子柱 Metrosep A Supp 5 和 7 行可靠保,使其不受品或淋洗液的染。它含有与 Metrosep A Supp 5 相同的分材料,也同由 PEEK(聚)制成,并直接以几乎无死点容的方式到相分柱上(«On Column Guard System»)。保柱将延分析用柱的使用寿命,且不会影其色分效率。建使用 A Supp 5 Guard/4.0,其价格惠且操作。

MiPT

用于安装 Dosino 以行局部循的附件。

858 Professional Sample Processor – Pump

858 Professional Sample Processor – Pump 可理体在 500 µL 至 500 mL 之的品。行品移,既可以使用内置的双向双通道蠕、也可通 800 Dosino 来行。

930 Combustion IC PP (AJ)

930 Combustion IC PP (AJ) 可使用在燃分解(高温水解)方法分析各可燃品中的素和硫,然后定子色(Combustion IC)。它包括所有需要的部件,如 Analytik Jena 的 Combustion Module(2.136.0700)、920 Absorber Module、930 Compact IC Flex Oven/SeS/PP/Deg 和 MagIC Net 件。必要,930 Metrohm Combustion IC-Paket 可附加一台 Autosampler(Autosampler MMS 5000) 用于固体和液体品。整套分析程包括品入和品分解均自化行,且由 MagIC Net 控制。

Autosampler MMS 5000 (AJ)

Analytik Jena(耶拿分析器公司)的 Autosampler MMS 5000 (AJ) 用于搭配 Metrohm Combustion IC 液和固品行全自分析。了根据正的品型模化的 Multi-Matrix 器行整,需使用液体用套件 (6.7303.000) 或固体用套件 (6.7302.000)。