Application Note AN-CIC-034

燃焼法イオンクロマトクラフィシステムによる水中のAOXの迅速分析

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

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).

EXPERIMENTAL

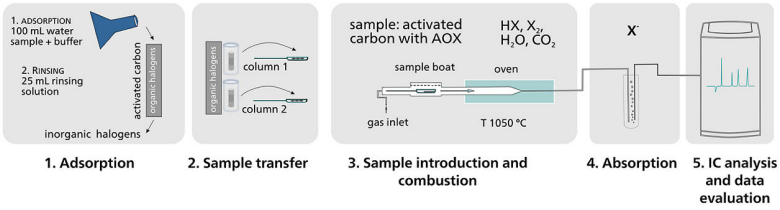

Figure 1. Schematic of the procedure for AOX (WP-081) and AOF (AN-CIC-033) analysis. The first step is adsorption performed with the APU sim (Analytik Jena) for semi-automated and standardized adsorption of up to six samples in parallel. After the second step of sample transfer into the combustion boats, 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).

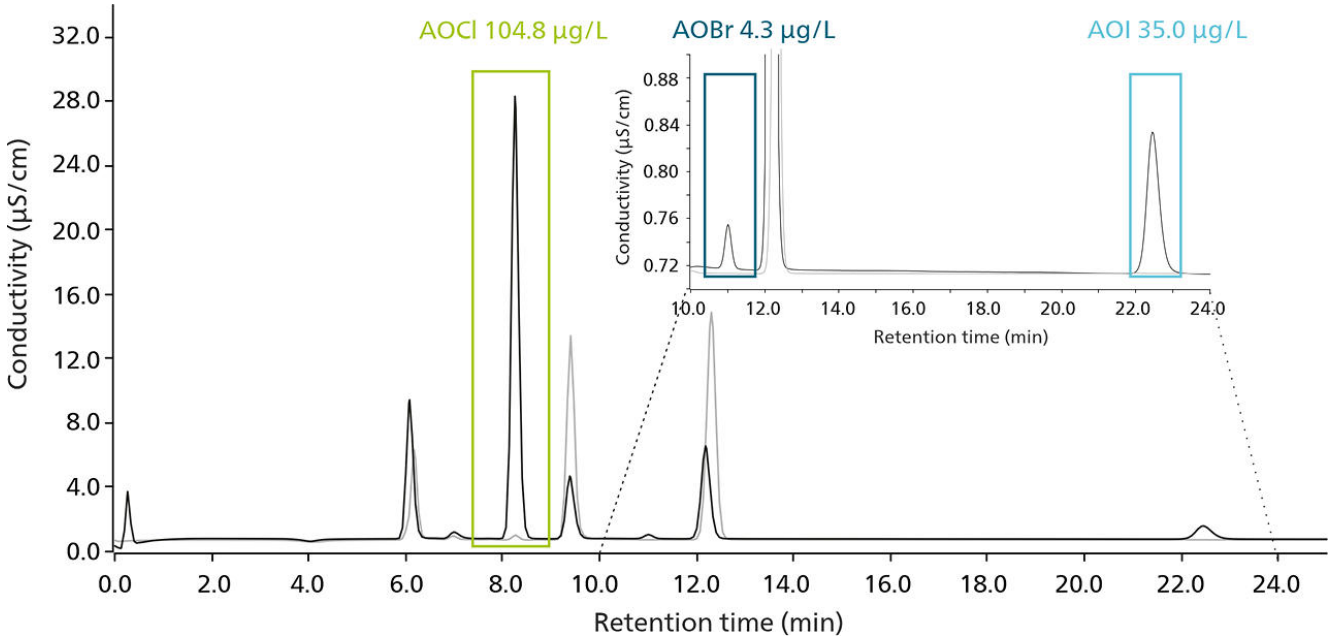

Figure 2. Chromatogram overlay of the blank and a wastewater sample for the determination of AOCl, AOBr, and AOI measured from absorption column #1. To calculate the mass concentration of the individual AOX fractions, blank correction was performed according to Equation 1. No halogens were adsorbed on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

1. Xu, R.; Xie, Y.; Tian, J.; et al. Adsorbable Organic Halogens in Contaminated Water Environment: A Review of Sources and Removal Technologies. *J Clean Prod* **2021**, 283.
2. Müller, G. Sense or No-Sense of the Sum Parameter for Water Soluble "Adsorbable Organic Halogens" (AOX) and "Absorbed Organic Halogens" (AOX-S18) for the Assessment of Organohalogens in Sludges and Sediments. *Chemosphere* **2003**, *52* (2), 371–379.
3. Dann, A. B.; Hontela, A. Triclosan: Environmental Exposure, Toxicity and Mechanisms of Action. *J Appl Toxicol* **2011**, *31* (4), 285–311.
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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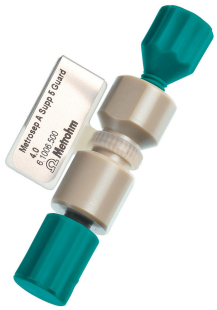
CONFIGURATION

Metrosep A Supp 5 - 250/4.0

困難な分離作業のための理論段数の極端に高い、メトローム社か開発した高性能分離カラム。複雑な分離問題も、Metrosep A Supp 5 - 250/4.0によって容易かつ再現可能に解決てきます。カラムの容量か高いのて、例えは、サンフル前処理なしの、150 mg/Lの塩化物、並ひに1 µg/Lの臭素酸塩の証明も可能てす。このカラムの適用範囲は、標準陰イオンの証明にととまりません。Metrosep A Supp 5 - 250/4.0は、半導体産業や発電所のホイラー給水における高い純度基準の確実な検査か重要な場合に選択されるカラムてす。

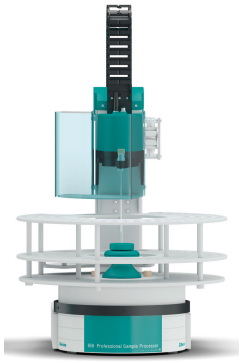


Metrosep A Supp 5 Guard/4.0

Metrosep A Supp 5 Guard/4.0は、IC陰イオンカラムMetrosep A Supp 5 および 7をサンフルや溶離液による汚れからしっかりと守ります。
これはMetrosep A Supp 5と同し分離材料を有し、また同様にPEEK製てあり、それぞれの分離カラムにほほテットホリュームなして直接取り付けることかてきます(「On Column Guard System」)。カートカラムは、クロマトクラフィーにおける分離性能に影響を与えることなく、分析用カラムの寿命を延はします。安価て取扱いか容易てあるため、A Supp 5 Guard/4.0の使用か大変推奨されています。

IC: MiPT

ハーシャルルーフインシェクションのトシーノ設置のための付属品セット。



858 Professional Sample Processor – Pump

858 フロフェッショナルサンフルフロセッサ - ホンフは、500 µLから500 mLまでのサンフルを処理します。サンフルは内蔵式双方向性の2チャンネルのヘリスタリックホンフまたは800 トシーノ電動ヒュレットによって転送されます。

930 Combustion IC PP (AJ)

930 Combustion IC PP (AJ)は、インライン燃焼消化(熱加水分解)により、またその後イオンクロマトクラフ測定(Combustion IC)を行うことによって、あらゆる種類の可燃性サンフル中のハロケンおよび硫黄の分析を可能にします。これは、Analytik Jena社の Combustion Module (2.136.0700)、920 Absorber Module 、930 Compact IC Flex Oven/SeS/PP/Deg、MagIC Net ソフトウェアなといった、必要とされるあらゆるコンホーネントを包括しています。930 Metrohm Combustion ICハッケーシは需要に応して固体または液体サンフルのためのオートサンフラーによって補完することかてきます(Autosampler MMS 5000)。サンフル注入およびサンフル分解を含む分析行程全体か完全に自動化され、MagIC Netによって完全に制御されます。

Autosampler MMS 5000 (AJ)

液体および固体のサンフルの完全自動分析のためメトローム燃焼法ICと共に使用されるAnalytik Jena社のAutosampler MMS 5000 (AJ)。モシュール方式のマルチ・マトリックス・サンフラーを正しいサンフルタイフに合わせるため、液体キット(6.7303.000)または固体キット(6.7302.000)の使用か必要となります。