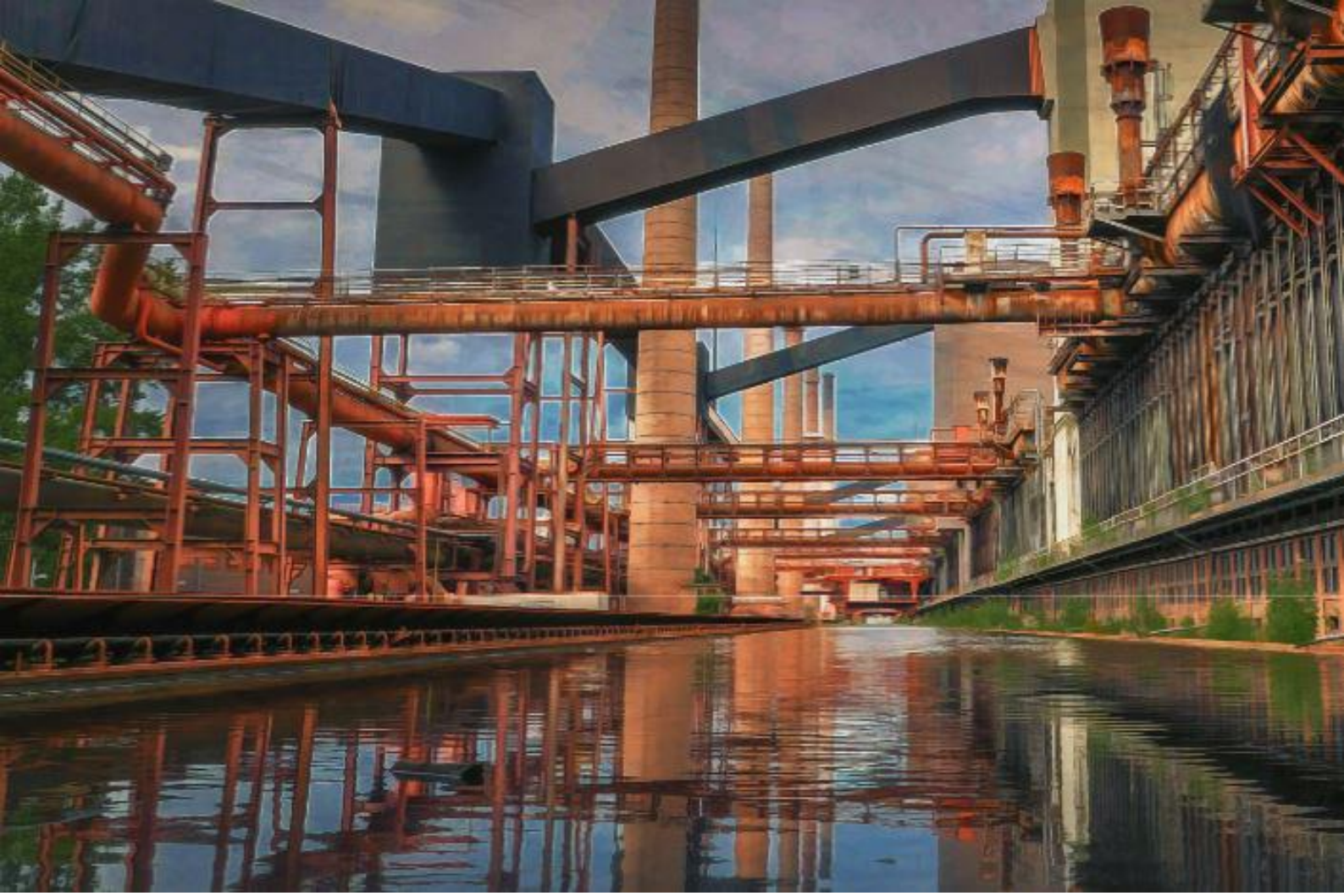


Application Note AN-CIC-034

Fast analysis of AOX in waters by CIC

Measurement of AOCl, AOBr, AOI, and AOF according to DIN 38409-59

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. The new **DIN 38409-59** describes a validated procedure of adsorption and analysis via **combustion ion chromatography (CIC)** to determine **AOCl**, **AOBr**, **AOI**, the sum parameter **CIC-AOX$_{(Cl)}$**, as well as **AOF**, a monitoring parameter for per- and polyfluorinated alkyl substances (PFASs) currently of emerging global concern. This Application Note explains the CIC method used to fulfill DIN 38409-59 for AOX and AOF analysis.

EXPERIMENTAL

This application is focused on the experimental approach of AOX and AOF analysis. More detailed information can be found in related Metrohm literature (WP-078, WP-081, AN-CIC-033). 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). AOF determination is now within the scope of the new DIN 38409-59, however the sample preparation for such samples requires neutralization. This is done by adding sodium nitrate to the samples (Table 1).

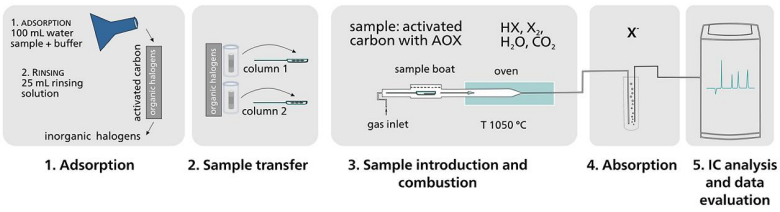


Figure 1. Schematic of the procedure for AOX and AOF analysis (WP-081). The first step is adsorption performed with the APU sim (Analytik Jena) for semi-automated and standardized adsorption of up to six samples in parallel. After the second step of sample transfer into the combustion boats, the sample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

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).

Table 1. Parameters for AOF and AOX 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	

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).

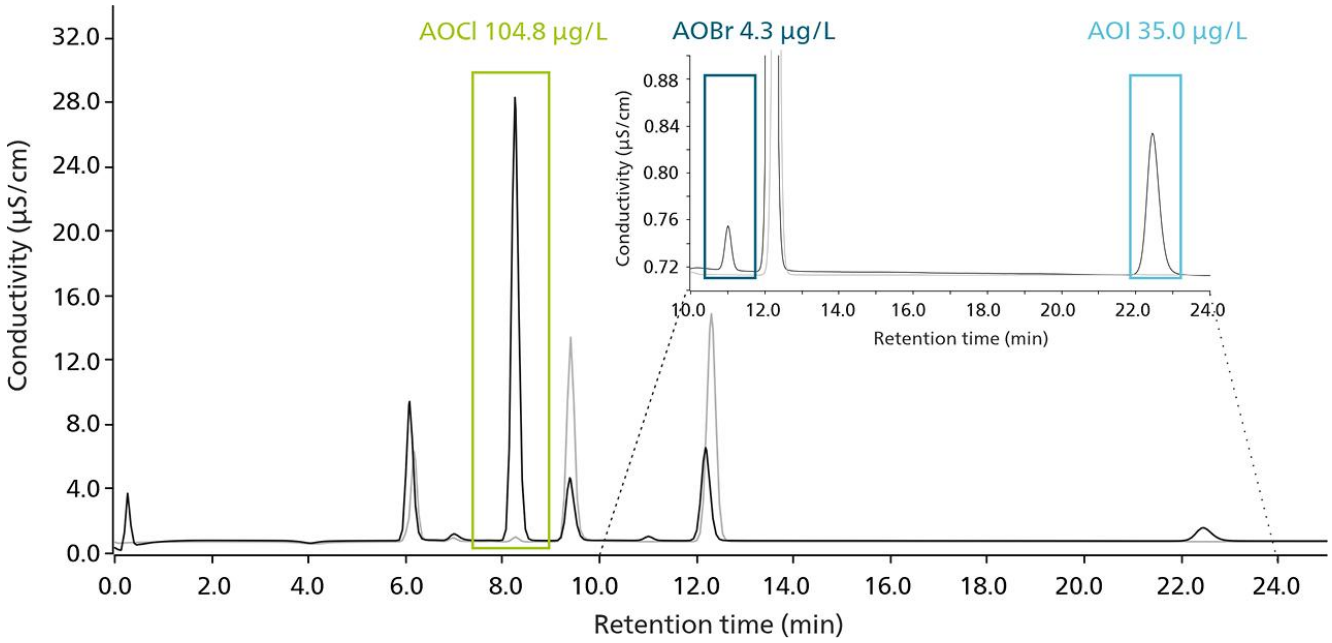


Figure 2. Chromatogram overlay of the blank and a wastewater sample for the determination of AOCl, AOBr, and AOI measured from absorption column #1. To calculate the mass concentration of the individual AOX fractions, blank correction was performed according to Equation 1. No halogens were adsorbed on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

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 and AOF 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).

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

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

RESULTS

Individual concentrations for AOCl, AOBr, and AOI, as well as for AOF from neutralized samples 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.

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

Equation 2.

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

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. 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 for full AOF/AOX procedure), 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 fractions contributing to the AOX contents (Figure 2, WP-081) and to assess AOF (AN-CIC-033, WP-078).

CONCLUSION

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

A significant advantage of DIN 38409-59 is that it allows the determination of adsorbable organically bound halogens as individual sum parameters (i.e., AOCl, AOBr, and AOI) and also provides a fast approach to assess total PFASs content using the validated approach for AOF. 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.

Internal reference: AW IC CH6-1438-042021

CONTACT

Metrohm France
13, avenue du Québec - CS 90038
91978 VILLEBON COURTABOEUF CEDEX
info@metrohm.fr

CONFIGURATION

Metrohm Combustion IC manuel quartz

Le kit Metrohm Combustion IC manuel quartz permet l'analyse d'halogènes et du soufre dans des échantillons combustibles de tout type à l'aide de la désagrégation par combustion inline (pyrohydrolyse) avec détermination par chromatographie ionique consécutive (Combustion IC). Il comprend tous les composants nécessaires, tels que le Combustion Oven (TEI) de Trace Elemental Instruments (2.0136.0600), le tube d'incinération en quartz (6.07311.100), le 920 Absorber Module, le 930 Compact IC Flex Oven/SeS/PP/Deg et le logiciel MagIC Net. Au besoin, le kit Metrohm Combustion IC peut etre complété par l'un des passeurs d'échantillons suivants : Solid Autosampler CIC (TEI), Liquid Autosampler CIC (TEI) ou GLS Sampler CIC (TEI).

Metrosep A Supp 5 - 250/4,0

La colonne de séparation haute performance de la maison Metrohm dispose d'un très grand nombre de plateaux pour les opérations de séparation les plus exigeantes. Meme les problèmes de séparation complexes peuvent etre résolus facilement et de manière reproductible grace à la colonne Metrosep A Supp 5 - 250/4.0. La haute capacité de cette colonne permet par ex. la détection de 1 µg/L de bromate en présence de 150 mg/L de chlorure sans aucune préparation des échantillons. Le spectre des applications possibles de cette colonne dépasse largement la seule détection des anions standard. La Metrosep A Supp 5 - 250/4,0 est la colonne de choix lorsqu'il s'agit de controler avec fiabilité de hauts niveaux de pureté dans l'industrie des semi-conducteurs ou dans l'eau d'alimentation de chaudières dans les centrales électriques.

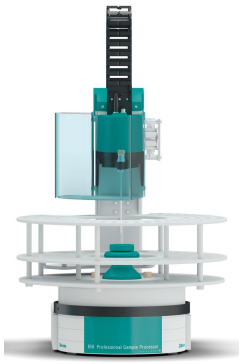
Metrosep A Supp 5 Guard/4,0

La Metrosep A Supp 5 Guard/4,0 protège la colonne CI pour anions Metrosep A Supp 5 et 7 de manière fiable contre les contaminations provenant des échantillons et de l'éluant.

Cette précolonne contient le meme matériau de séparation que la Metrosep A Supp 5, est comme elle fabriquée en PEEK et directement vissée sur la colonne de séparation correspondante, pratiquement sans volume mort, selon le système « On Column Guard ». La précolonne prolonge la durée de vie de la colonne analytique sans altérer pour ainsi dire sa performance de séparation chromatographique. Son prix avantageux et sa facilité de manipulation font que l'utilisation de la A Supp 5 Guard/4,0 est souvent recommandée.

Équipement CI : MiPT

Jeu d'accessoires pour le montage d'un Dosino pour Partial-Loop-Injection.



858 Professional Sample Processor – Pump

Le 858 Professional Sample Processor – Pump traite des échantillons de 500 µL à 500 mL. Le transfert des échantillons s'opère soit au moyen de la pompe péristaltique bidirectionnelle à deux voies intégrée soit par un 800 Dosino.