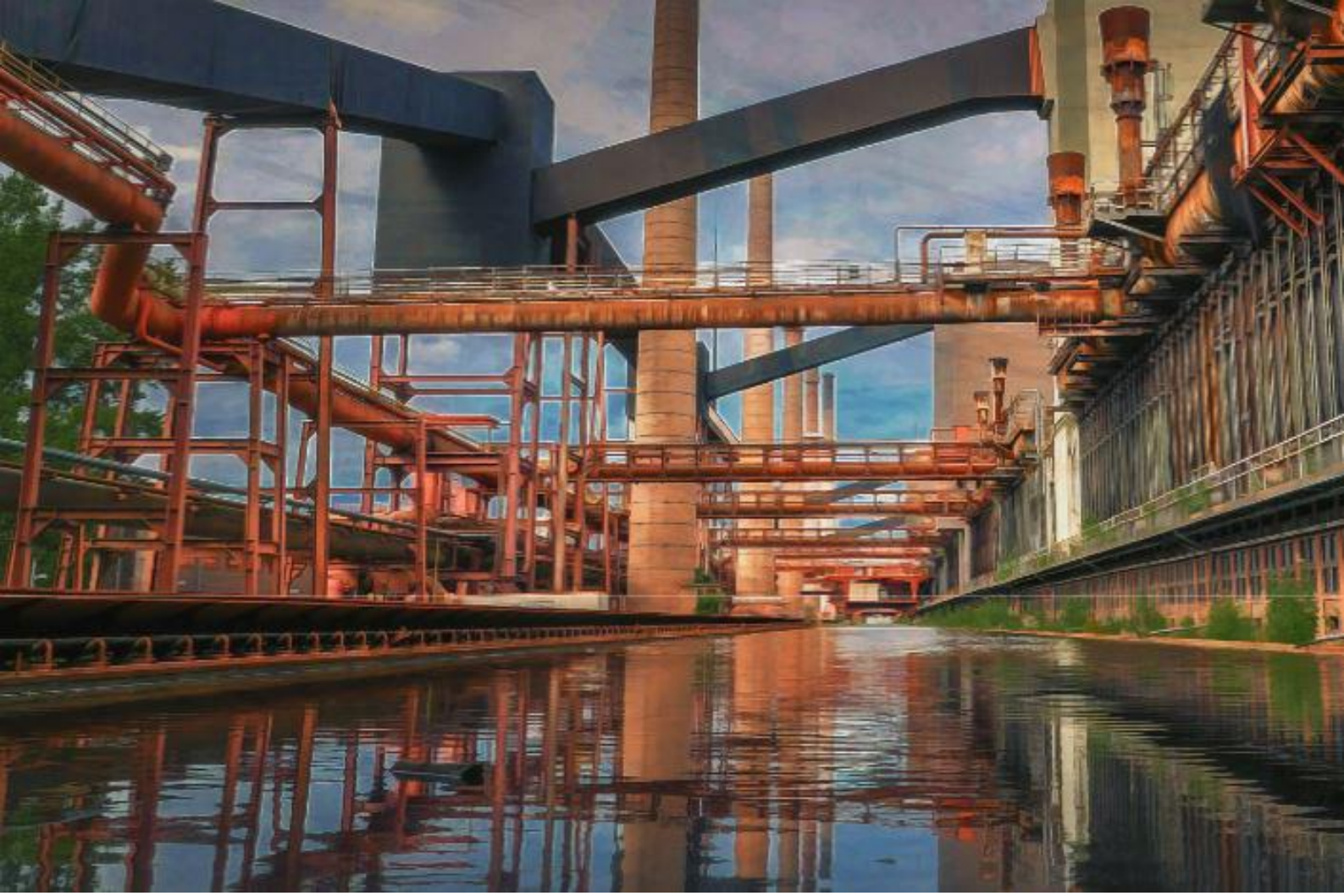

Application Note AN-CIC-034

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).

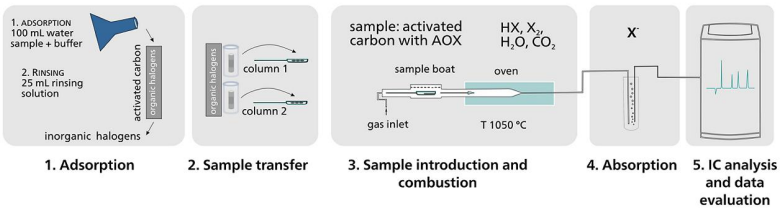

Figure 1. Schematic of the procedure for AOX and AOF analysis (WP-081). The first step is adsorption performed with the APU sim (Analytik Jena) for semi-automated and standardized adsorption of up to six samples in parallel. After the second step of sample transfer into the combustion boats, the sample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

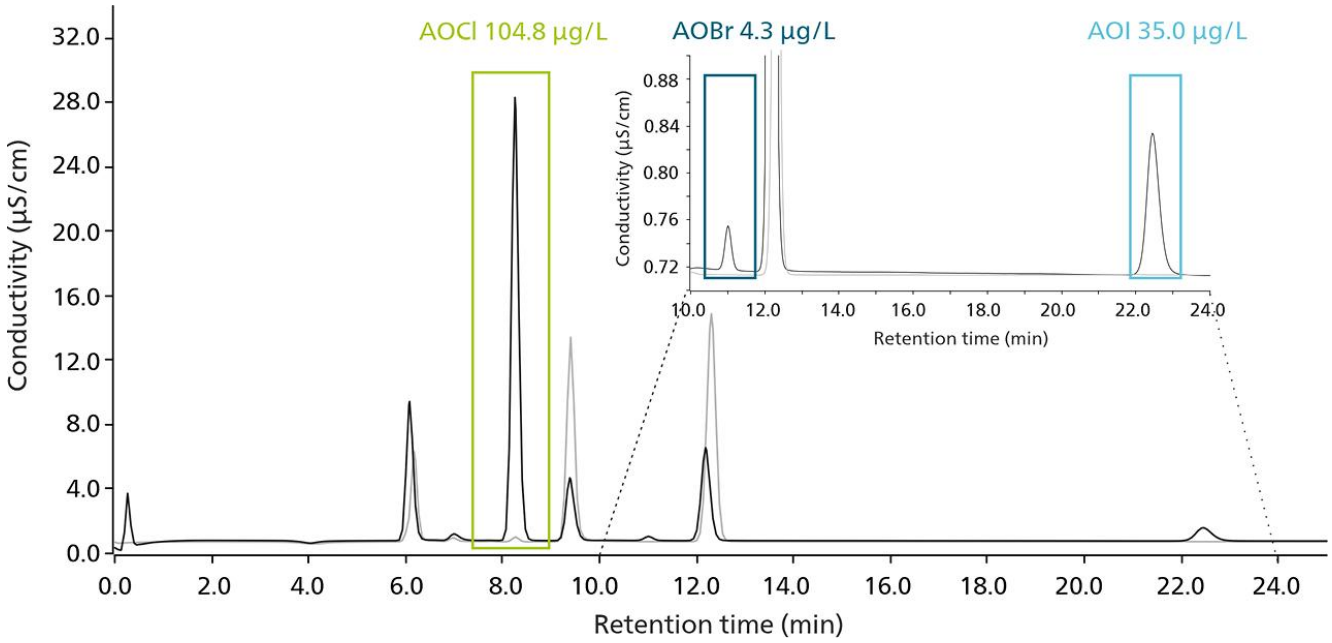

Figure 2. Chromatogram overlay of the blank and a wastewater sample for the determination of AOCl, AOBr, and AOI measured from absorption column #1. To calculate the mass concentration of the individual AOX fractions, blank correction was performed according to Equation 1. No halogens were adsorbed on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

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CONFIGURATION

Metrohm Combustion IC Manual - Quartz

The Metrohm Combustion IC Manual - Quartz package enables the analysis of halogens and sulfur in flammable samples of all types using inline combustion digestion (pyrohydrolysis) with subsequent ion chromatography determination (Combustion IC). It comprises all required components, such as the Combustion Oven (TEI) from Trace Elemental Instruments (2.0136.0600), the quartz combustion tube (6.07311.100), the 920 Absorber Module, the 930 Compact IC Flex Oven/SeS/PP/Deg, and the MagIC Net software. If necessary, the Metrohm Combustion IC package can be supplemented with one of the following Autosamplers: Solid Autosampler CIC (TEI), Liquid Autosampler CIC (TEI) or GLS Sampler CIC (TEI).

Metrosep A Supp 5 - 250/4.0

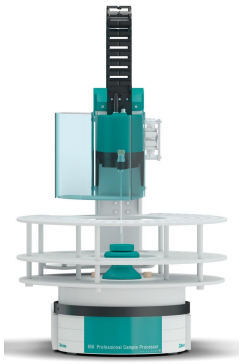
The high-performance separation column from Metrohm with an extremely high number of plates for the most demanding separation tasks. Even complex separation problems can be solved easily and reproducibly with the Metrosep A Supp 5 - 250/4.0. The high capacity of the column allows, for example, the detection of 1 µg/L bromate along with 150 mg/L chloride without sample preparation. The range of applications possible with this column far exceeds the detection of standard anions. The Metrosep A Supp 5 - 250/4.0 is the column of choice when it comes to reliable monitoring of the high purity standards in the semiconductor industry or of the boiler feed water of power plants.

Metrosep A Supp 5 Guard/4.0

The Metrosep A Supp 5 Guard/4.0 reliably protects the Metrosep A Supp 5 and 7 IC anion columns against contamination from the sample or the eluent. It contains the same separation material as the Metrosep A Supp 5, is also made of PEEK, and is screwed directly onto the respective separation column with virtually no dead volume ("On Column Guard System"). The guard column prolongs the service life of the analytical column, with practically no influence on its chromatographic separating efficiency. The economical price and simple handling make using the A Supp 5 Guard/4.0 highly recommended.

IC equipment: MiPT

Accessory set for assembling a Dosino for Partial-Loop-Injection.



858 Professional Sample Processor – Pump

The 858 Professional Sample Processor – Pump processes samples from 500 µL to 500 mL. The sample transfer takes place either with the installed bidirectional two-channel peristaltic pump or with an 800 Dosino.