Application Note AN-CIC-033

Monitoring PFASs in water sources

Non-targeted adsorbable organically bound fluorine (AOF) analysis by CIC

Per- and polyfluorinated alkyl substances (PFASs) are thousands of organic molecules in which all the hydrogen atoms on at least one carbon are replaced by fluorine [1]. PFASs are widely used in different industries, e.g., as surfactants for film-forming foams or as impregnating agents for packaging [2]. Due to their extreme persistence, they are called «forever chemicals», as longer chain compounds accumulate in the environment and biomagnify [3]. Negative health impacts have forced governmental and standardization bodies to take action against the most harmful PFASs, but suitable analytical techniques to trace and regulate these chemicals are needed. Targeted analysis of PFASs is complex and requires expensive instrumentation [4]. Conversely, determining non-targeted sum parameters is an easier way to screen for PFASs. **Adsorbable organically bound fluorine** (AOF) is a sum parameter covering a broad spectrum of organofluorines. AOF analysis is an adequate screening method for PFASs in water. DIN 38409-59 describes how to use the combination of **pyrohydrolytic combustion** and **ion chromatography** (CIC) for AOF analysis – for which Metrohm provides a robust and reliable solution.

SAMPLE AND SAMPLE PREPARATION

Three different aqueous environmental samples—one surface water and two waste waters—were analyzed for their AOF content following the procedure given in DIN 38409-59.

In contrast to other adsorbable organically bound halogens (i.e., AOCl, AOBr, and AOI), it is crucial for the determination of AOF that the samples have a neutral pH to avoid absorption of inorganic fluorine. Therefore, the samples were prepared by adding 0.5 mL of a 2 mol/L sodium nitrate solution to 100 mL sample. The adsorption of organofluorine was achieved on activated carbon as an automated sample preparation step (APU sim, Analytik Jena). Automation makes it a standardized preparation method with excellent repeatability and a high sample throughput. In short, two carbon cartridges connected in series are flushed with 100 mL sample with a flow rate of 3 mL/min. After adsorption, the two carbon cartridges are washed with 25 mL of a 0.01 mol/L sodium nitrate solution at a flow rate of 3 mL/min. After finishing the sample preparation, the complete content of the two cartridges is transferred into two separate ceramic boats for analysis by CIC.

EXPERIMENTAL

The activated carbon containing all adsorbable organically bound fluorine is analyzed by pyrohydrolytic combustion. The CIC system consists of an autosampler for solid samples, a combustion module, an absorber module, and an ion chromatograph (IC) (Figure 1).

Figure 1. Combustion IC setup consisting of a 930 Compact IC flex (2.930.2560), a 920 Absorber Module (2.920.0010), a Combustion Module (Oven + ABD, 2.136.0700), and a MMS 5000 Autosampler (2.136.0800) configured for solid samples (6.7302.000).

The autosampler automatically transfers the sample boats into the combustion module, where they are combusted at a temperature of 1050 °C. With the gas stream, volatilized fluorine (next to other halogens and sulfur) is transferred into the 920 Absorber Module and absorbed into the aqueous phase. Precise and automated liquid handling is done with Dosinos, transferring the aqueous sample into the IC (930 Compact IC flex) for analysis. To keep the background and limits of detection of fluorine low, it is essential to use clean chemicals which are at least of the purity grade «per analysis».

The separation of fluoride (retention time 6.2 minutes) from other halogens is achieved on a Metrosep A Supp 5 - 250/4.0 column in combination with the A Supp 5 Guard/4.0 (Figure 2).

Automated eluent production with the 941 Eluent Production Module enables continuous and almost unattended operation of the CIC, increasing the overall performance and analysis efficiency.

The calibration (0.01–0.5 mg/L) was performed automatically from one standard solution (sodium fluoride, 0.5 mg/L) applying the Metrohm intelligent Partial Loop Injection Technique (MiPT). A calibration range of 0.01–0.5 mg/L was achieved by the using one standard with different injection volumes (4–200 µL).

The method detection limit and the method performance were checked with standardized reference materials (4-fluorobenzoic acid) and blanks (ultrapure water) prepared in the same way as the samples and analyzed for their AOF content.

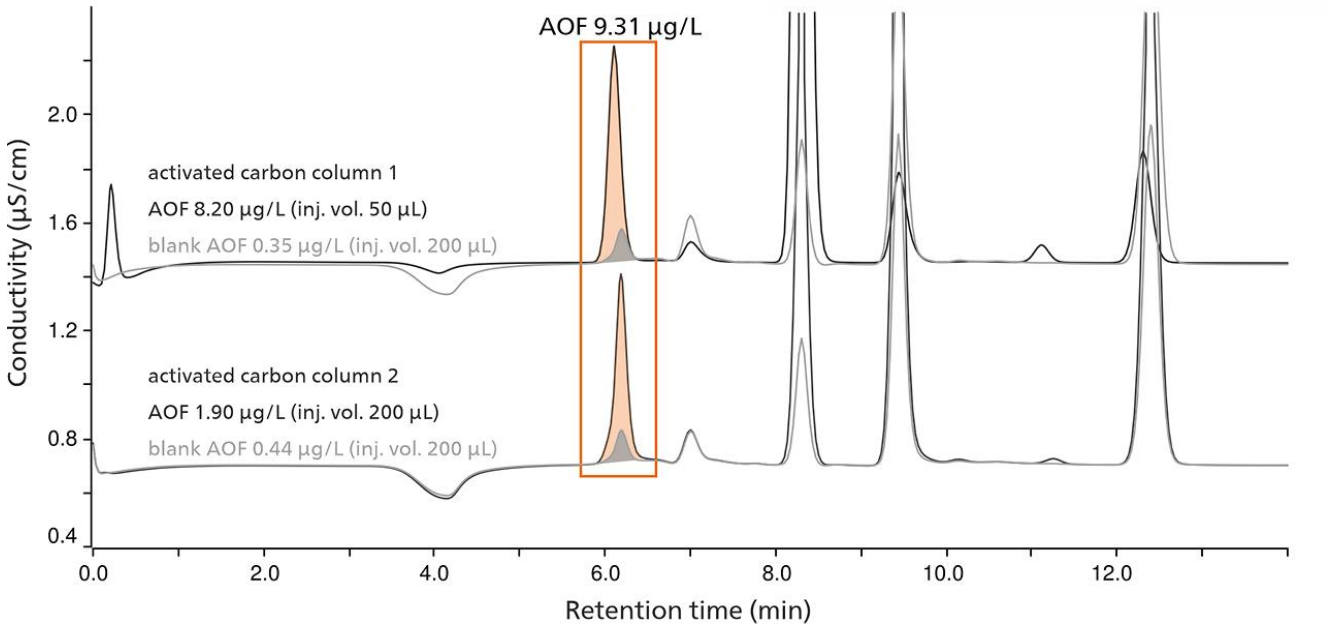

Figure 2. Chromatograms for a wastewater sample. An AOF concentration of 7.85 µg/L was found on the first carbon column and 1.46 µg/L on the second carbon column. This adds up to a total AOF concentration of 9.31 µg/L for this sample. This is the result after blank subtraction. The respective AOF blanks are also shown in grey.

The final sample concentrations are calculated according to the formula below. Thereby the final AOF concentration is the sum of the content measured for the two subsequent cartridges after blank subtraction (Figure 2).

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

c(AOF)	Mass concentration of AOF in µg/L
$c(F^-)_{IC}$	Fluoride concentration in the sample's absorption solution in µg/L
V_{Abs}	Final volume of the absorption solution in L
V_{Smpl}	Volume of the sample that was used for adsorption in L
$c(F^-_{BW})_{IC}$	Fluoride 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 in L

RESULTS

All samples were analyzed in replicates (n=4). All waters contained trace concentrations of AOF ranging from an average of 6.52 µg/L to 9.70 µg/L, with lower concentrations found in surface water compared to wastewater (Table 1). Although concentrations of AOF are generally low and sample preparation can be complex, the automation of sample processing and the analysis guarantees excellent repeatability. For the replicates, RSDs of 3.6–5.3% were achieved (n=4).

For routine analysis, the method blank was determined to be 1.1 µg/L for AOF (based on ultrapure water and including all sample preparation and combustion steps).

Table 1. Results of the AOF analyses for surface water and wastewater samples. The table shows AOF results for the four measured replicates of each sample, the average and standard deviation (SD), and the relative standard deviation (RSD) as determined with the formula shown above. The AOF concentrations are corrected for the blank content as required by DIN 38409-59.

Sample	AOF #1 (µg/L)	AOF #2 (µg/L)	AOF #3 (µg/L)	AOF #4 (µg/L)	Average ± SD (µg/L)	RSD (%)
Surface water	6.26	6.27	6.79	6.77	6.52±0.30	4.6
Wastewater 1	10.23	10.03	9.31	9.21	9.70±0.51	5.3
Wastewater 2	7.36	6.99	7.61	7.21	7.29±0.26	3.6

CONCLUSION

Determination of the sum parameter **AOF** according to **DIN 38409-59** enables fast and reliable **screening of PFASs** in various water samples. Ideal for monitoring, this approach can serve as a supplementary method to the comprehensive, time-consuming, and expensive targeted analysis of PFASs by e.g., LC-MS/MS. With the possibility of automated sample preparation in combination with a fully automated analysis by CIC, this is an easy, reliable, fully automated, and straightforward technique for routine AOF analysis. AOF analysis with CIC according to DIN 38409-59 is thus a fast method to monitor PFASs in water sources.

Aside from AOF, DIN 38409-59 also describes the analysis of adsorbable organically bound halogens **chlorine (AOCl)**, **bromine (AOBr)**, and **iodine (AOI)**, and the **sum of the adsorbable organically bound halogens (CIC-AOX$_{(Cl)}$)** with the same system setup and method parameters. This additionally enables laboratories to report individual, fast, and reliable results for all of these components.

REFERENCES

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Internal reference: AW IC CH6-1438-042021

CONTACT

Metrohm Viet Nam
Phan Dinh Giot
70000 Ho Chi Minh
info@metrohm.vn

CONFIGURATION

930 Combustion IC PP (AJ)

The 930 Combustion IC PP (AJ) 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, e.g., the Combustion Module from Analytik Jena (2.136.0700), the 920 Absorber Module, the 930 Compact IC Flex Oven/SeS/PP/Deg, and the MagIC Net software. If necessary, the 930 Metrohm Combustion IC package can be supplemented with an Autosampler for solid or liquid samples (MMS 5000 Autosampler). The entire analysis, including sample input and sample digestion, is completely automated and is completely controlled by MagIC Net.

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.

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.

930 Compact IC Flex Oven/SeS/PP/Deg

The 930 Compact IC Flex Oven/SeS/PP/Deg is the intelligent Compact IC instrument with **column oven**, **sequential suppression**, **peristaltic pump** for suppressor regeneration and built-in **degasser**. The instrument can be used with any separation and detection methods.

Typical areas of application:

- Anion or cation determinations with sequential suppression and conductivity detection

920 Absorber Module

The 920 Absorber Module combines the Combustion Module with the ion chromatograph. The 920 Absorber Module ensures that the gaseous compounds of the analytes are dissolved and channeled to the IC. It is responsible for the entire Liquid Handling. In addition to Combustion IC, it can also be used for gas analysis.

MMS 5000 Autosampler (AJ)

Autosampler MMS 5000 (AJ) made by Analytik Jena for use with the Metrohm Combustion IC for fully automatic analysis of liquid and solid samples. To adapt the modular Multi-Matrix sampler to the correct sample type, either the liquids kit (6.7303.000) of the solids kit (6.7302.000) must be used.