Application Note AN-CIC-033

# Monitoring PFASs in water sources

## Determining adsorbable organically bound fluorine (AOF) in aqueous matrices according to U.S. EPA Method 1621

**Per- and polyfluorinated alkyl substances (PFASs)**, a group of thousands of organic molecules, are widely used in different industries (e.g., as surfactants for film-forming foams or as impregnating agents for packaging) [1,2]. Due to their extreme persistence, they are called «forever chemicals», accumulating in the environment and biomagnifying [3]. Negative health impacts have forced governmental and standardization bodies to take action against the most harmful PFASs. The determination of the non-targeted sum parameter AOF (adsorbable organic fluorine, also called adsorbable organically bound fluorine) is an easy, straightforward way to screen for PFASs. AOF is a sum parameter covering a broad spectrum of organofluorines. Based on the same principle, i.e., adsorption of organic fluorines on a carbon cartridge, pyrohydrolytic combustion, and determination of fluorine by ion chromatography, the standardization bodies U.S. EPA (U.S. EPA Method 1621), DIN (DIN 38409-59), and ISO (ISO/DIS 18127) developed appropriate analytical approaches to estimate a screening level for «total» PFASs in aqueous matrices. This Application Note focuses on the described analytical approach for AOF analysis by combining **pyrohydrolytic combustion** and **ion chromatography (CIC)**.

## SAMPLE AND SAMPLE PREPARATION

Three different aqueous environmental samples—one surface water and two waste waters—were analyzed for their AOF content, as described below.

In contrast to other adsorbable organically bound halogens (i.e., chlorine – AOCl, bromine – AOBr, and iodine – AOI), it is crucial for the determination of AOF that the samples have a neutral pH to prevent absorption of any inorganic fluorine. Therefore, each 100 mL sample was pretreated with 0.5 mL of a 2 mol/L sodium nitrate solution.

Organofluorine adsorption was achieved on activated carbon as an automated sample preparation step (APU sim, Analytik Jena). Automation standardizes the preparation method resulting in excellent repeatability and allows for a high sample throughput. In this step, 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).

The autosampler automatically transfers the ceramic sample boats into the combustion module, where they are combusted at 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, automated liquid handling is done using Dosinos to transfer 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 chemical reagents which are at least of the purity grade «per analysis».

## EXPERIMENTAL

**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 an MMS 5000 Autosampler (2.136.0800) configured for solid samples (6.7302.000).

The separation of fluoride (retention time 6.2 minutes) from other halogens is achieved on a Metrosep A Supp 5 - 250/4.0 separation 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) by applying the Metrohm intelligent Partial-Loop Injection Technique (MiPT). By injecting one standard with different injection volumes (4–200 µL), a calibration range of 0.01–0.5 mg/L was achieved.

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.

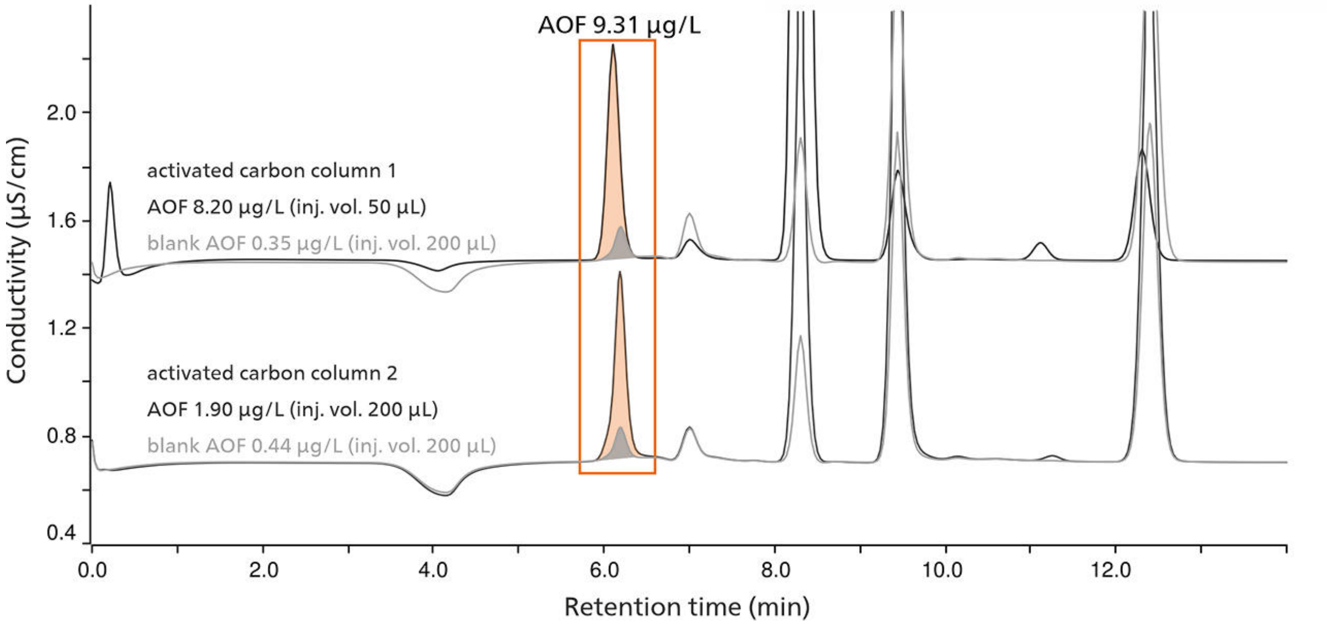

**Figure 2.** Chromatograms for a wastewater sample. An AOF concentration of 7.85 µg/L was found on the first carbon column and 1.46 µg/L on the second carbon column. This adds up to a total AOF concentration of 9.31 µg/L for this sample. This is the result after blank subtraction. The respective AOF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

| 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 | 4.56 | 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 |

Determination of the sum parameter **AOF** by adsorption of organic fluorine, pyrohydrolytic combustion, and subsequent fluorine determination by ion chromatography as described in **U.S. EPA 1621**, **DIN 38409-59**, and **ISO/DIS 18127** enables a fast and reliable way for **screening 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 [**4**]. With the possibility of automated sample preparation in combination with fully automated analysis by CIC, this is an easy, reliable, economic, time-saving, and straightforward technique for routine AOF analysis and estimation of «total» PFASs.

## REFERENCES

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