

# AOF by combustion IC – non-targeted complementary determination of PFAS in aqueous samples

Authors: Eleonora von Abercron, Udo Neist, Inge Klocke, Dr. Sebastian Georgii, Prof. Dr. Hubertus Brunn  
Hessian State Laboratory,  
Wiesbaden, Germany

Dr. Detlef Jensen  
Thermo Fisher Scientific GmbH,  
Dreieich, Germany

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## Goal

To develop an automated method to determine a range of perfluorinated alkyl substances (PFAS) by combustion IC within environmentally relevant matrices and compare the results with existing highly specific methods based on liquid chromatography mass spectrometry (LC-MS/MS)

## Introduction

PFAS are human-made chemicals, which have been manufactured since the 1940s. The most well-known PFAS compounds, perfluorooctanoic acid (PFOA) and



perfluorooctanesulfonic acid (PFOS), have been extensively studied for their chemical properties and toxicological effects. PFAS are used in a wide variety of consumer products, such as nonstick cookware, food containers, stain- and water-repellent fabrics, polishes, waxes, paints, and cleaning products. Other sources of PFAS are firefighting foams, which are primary groundwater contaminants at airports and military bases. Further environmental exposure to PFAS comes from industrial production facilities (e.g., chrome plating, electronics, manufacturing, or oil recovery). Living organisms, including plants, animals, and humans, can accumulate PFAS compounds in their tissue, which can build up over time and impact their health.<sup>1-3</sup>

Several national and international standardization and regulatory bodies have developed methods specifically for the determination of PFAS in aqueous samples.<sup>4-6</sup> These methods are mostly based on solid-phase extraction (SPE) followed by LC-MS/MS detection for only a select number of PFAS.

With the number of environmentally relevant fluoroorganic compounds and precursors that cannot yet be analyzed continuing to increase,<sup>7-10</sup> there is a need to restrict the release of these substances into the environment and develop suitable analytical methods for their detection. As such, German authorities have established regulatory requirements for various PFAS, chlorinated and brominated organics, and adsorbable organically bound halogens (AOX).<sup>11,12</sup> Many PFAS and their precursors, and fluorinated pharmaceuticals, for example, are not accounted for by the existing analytical methods. As a result, there is a growing need for a single analytical workflow that would allow for a direct determination of as many PFAS as possible.

Conventional ion chromatography (IC) cannot directly analyze non-ionic PFAS. Automated combustion ion chromatography (CIC), however, is used to determine organic halogen contaminants, such as AOX.<sup>13</sup> In CIC, the samples are oxidized by O<sub>2</sub> at elevated temperatures. As shown in Figure 1, pyrolysis takes place at temperatures exceeding 950 °C. Sulfur-containing compounds are oxidized to sulfur dioxide (SO<sub>2</sub>), and halogen-containing

substances form hydrogen halides (HX) or elemental halogens (X<sub>2</sub>). Loss of hydrogen fluoride through the reaction with the oven liner (quartz glass or ceramic) is avoided by continuously adding water during combustion (hydrolysis). The volatile pyrolysis products are then absorbed into an aqueous solution and subsequently detected as sulfates and halides (e.g., fluoride) by IC.<sup>14-17, 28</sup>

In contrast to the conventional titrimetric AOX methods, where only the sum of organic halogens is measured, the CIC approach provides halogen speciation as well as additional information about the adsorbable organic fluor-containing compounds.

This method can be considered a combination of several existing methods for organic-halogen measurement.<sup>18-20</sup> Halogen-containing organics from aqueous samples are adsorbed on activated carbon. The activated carbon is washed to remove inorganic halides. Sample and adsorbent are combusted, and the volatile oxidation products are absorbed in deionized (DI) water. This solution is subsequently analyzed by IC. A corresponding DIN standard using CIC is under development.<sup>21</sup>

This work focuses on PFAS, and the adsorbable organically bound fluorine (AOF). The use of this technique is well-documented for the determination of other adsorbable organic halogen-containing components (AOX).<sup>13,21,22</sup>

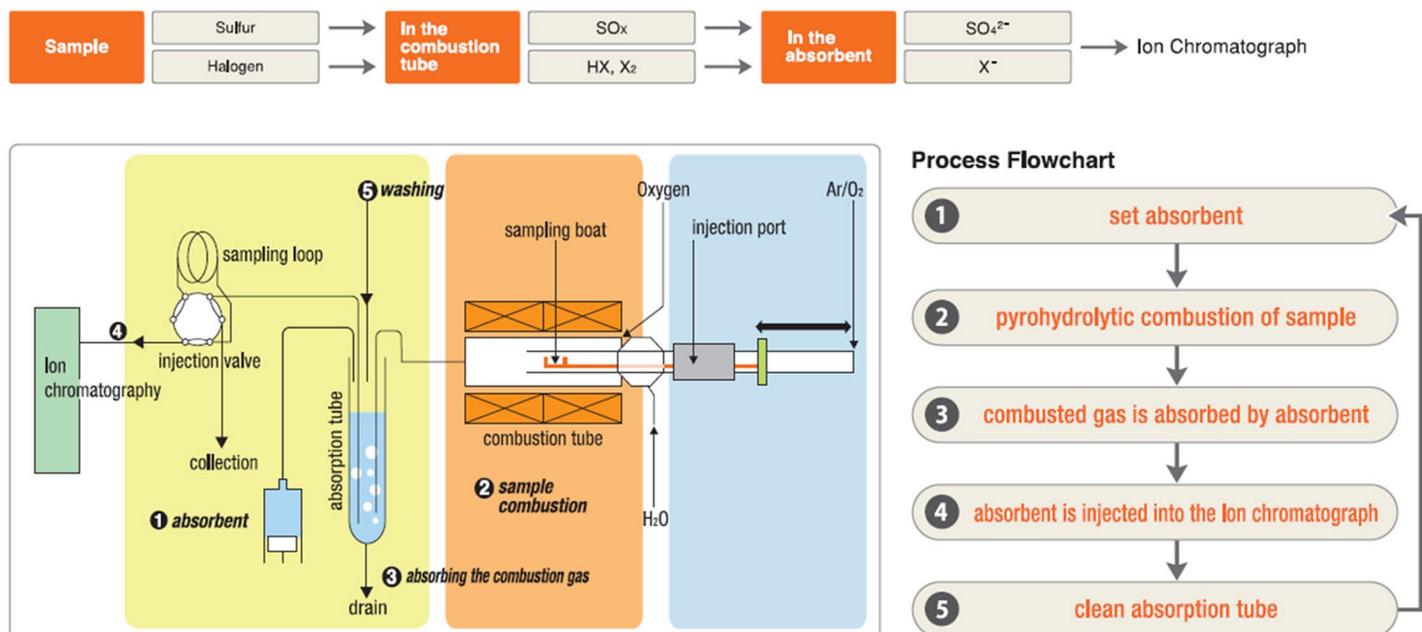


Figure 1. Diagram of a CIC system for the determination of adsorbable organic halogens<sup>23</sup>

## Experimental

### Equipment and supplies

- Thermo Scientific™ Dionex™ ICS-2100 Integrated Reagent-Free™ Ion Chromatography (RFIC™) system\*, including:
  - Isocratic Pump
  - Vacuum Degasser
  - Conductivity Cell and Detector
- Mitsubishi Chemical Analytech Automatic Combustion Unit Model AQF-2100H system, including:
  - Autosampler ASC-240S
  - Horizontal Furnace Model HF-210
  - Gas Absorption Unit GA-210

\* This application can be performed on any Thermo Scientific™ Dionex™ RFIC instrument.

### IC consumables

- Thermo Scientific™ Dionex™ EGC III KOH Eluent Generator cartridge ([P/N 074532](#))
- Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column ([P/N 060477](#))
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 2 mm ([P/N 082541](#))
- Thermo Scientific™ Dionex™ IonPac™ AS20 column, 2 × 250 mm ([P/N 063065](#))
- Thermo Scientific™ Dionex™ IonPac™ AG20 guard column, 2 × 50 mm ([P/N 063066](#))

### Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2.9
- Mitsubishi NSX-2100 software, version 2.1.6.0

For installation and software set-up, follow the procedure described in Technical Note 72211.<sup>24</sup>

### Sample adsorption system

Adsorption of organic halogen compounds was performed according to ISO 9562<sup>25</sup> automatically with an AutoAD SPE module (a1-envirosciences GmbH, Düsseldorf, Germany). Commercially available, ready-to-use columns, packed with activated carbon (AOXpack Premium, a1 envirosciences GmbH, Düsseldorf, Germany), are used instead of manually filled cartridges or columns. This saves time during sample preparation, increases reproducibility, and allows full automation of the sample preparation step.

### Reagents and standards

- Deionized (DI) water,  $\geq 18 \text{ M}\Omega\cdot\text{cm}$  at 25 °C
- Nitric acid (65%, Merck KGaA, Darmstadt, Germany)
- Sodium nitrate (99.5%, VWR Chemicals, Germany)
- Ammonium perfluorobutanesulfonate (PFBS) (98%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany)
- 4-Fluorobenzoic acid ( $\geq 98\%$ , Merck KGaA, Darmstadt, Germany)
- 1000 mg/L fluoride-calibrant solution (Merck KGaA, Darmstadt, Germany) for calibration of the IC
- Oxygen (O<sub>2</sub> 4.5, Praxair Germany GmbH, Düsseldorf)
- Argon (Ar 5.0, Praxair Germany GmbH, Düsseldorf)

## IC conditions

Parameter	Value
IC system	Dionex ICS-2100
Columns	Dionex IonPac AG20 (2 × 50 mm) and Dionex IonPac AS20 (2 × 250 mm)
Eluent source	Dionex EGC III KOH Eluent Generator cartridge with Dionex CR-ATC trap column
KOH gradient	Inject (0 min) 2 mM (0–0.1 min) 2–3 mM (0.1–5 min) 3–12 mM (5–21 min) 12 mM (21–24 min) 12–35 mM (24–25 min) 35 mM (25–28 min) 35–100 mM (28–28.2 min) 100 mM (28.2–32.2 min) 2 mM (32.2–32.4 min)
Run time	44 min
Flow rate	0.25 mL/min
Injection volume	250 µL
Temperature	30 °C (column temperature) 35 °C (detector cell temperature)
Backpressure	~2200 psi (100 psi = 0.6894 MPa)
Suppressed conductivity detection	Dionex AERS 500 suppressor (2 mm), timed constant current mode: 8 mA (0–28 min) 22 mA (28–33.2 min) 62 mA (33.2–37.4 min) 8 mA (37.4–44 min)
Background conductance	<0.5 µS/cm

## Combustion conditions

Parameter	Value
Furnace inlet temperature	950 °C
Furnace outlet temperature	1000 °C
Argon flow (carrier)	100 mL/min
Oxygen flow (combustion agent)	300 mL/min
Humidified argon flow	100 mL/min
Water supply scale	2
Pyrolysis tube	Quartz tube with ceramic insert and quartz wool
Sample boat	Ceramic
Absorption solution	Water
Final absorption solution volume	15 mL
AQF mode	Constant Volume
Automatic boat controller combustion program	Table 1

**Table 1. Autosampler ASC -240S combustion program**

Position (mm)	Wait time (s)	Speed (mm/s)
100	60	10
End	600	10
Cool	60	20
Home	200	20

## Sampling

Surface water, municipal wastewater, industrial wastewater, and groundwater samples were transported to the laboratory in amber glass bottles (1000 mL) at  $5 \pm 3$  °C. The samples were stored after stabilization with 2 mL HNO<sub>3</sub> (65%, pH < 2) at  $5 \pm 3$  °C until testing.

Comment: The latest results of our ongoing evaluation indicate that the sample acidification could be avoided.

## Sample preparation and measurement

Sample preparation was performed according to ISO 9562<sup>25</sup>. A sodium nitrate solution (5 mL, 0.2 M) was added to 100 mL of the unfiltered, acidified sample. A 100 mL aliquot of this solution was pumped at a flow rate of 3 mL/min through two activated carbon columns in series. The samples were processed undiluted unless the AOF concentration exceeded the calibrated concentration range (e.g., industrial wastewater samples). During this step, inorganic fluoride may adsorb to the column and contribute to false-positive AOF levels. Inorganic fluoride is removed by rinsing the column with 25 mL of a diluted sodium nitrate solution (0.01 M). The composition and pH of this rinsing solution may be reviewed and updated in the future, according to recent findings<sup>21</sup>. The contents of both adsorption columns were transferred to a ceramic sample boat, which was then automatically moved into the furnace where the activated carbon and the adsorbed substances were oxidized at 1000 °C in a stream of oxygen and argon. The volatile oxidization products were absorbed by 15 mL DI water and analyzed using IC. Each sample was combusted and analyzed in duplicate and was followed by two CIC blank values obtained from samples consisting of only DI water. An aliquot of the absorption solution was injected onto the analytical IC column. Separation, detection, and peak evaluation were carried out according to ISO 10304-1.<sup>18</sup>

## Results and discussion

### Calibration, linearity, and analytical performance

The linearity of the calibration function within the range of 2 to 500  $\mu\text{g/L}$  fluoride was evaluated according to the “point to point-slope” approach described in DIN 38402-51.<sup>26</sup> Before each sequence, the system was calibrated for the range between 2 to 100  $\mu\text{g/L}$  fluoride. At a minimum, a 5-point external standard calibration was carried out for fluoride. The calibration solutions were prepared from the individual standard stock solution through successive dilution. Table 2 shows an example of calibration data obtained from a multi-level calibration (2  $\mu\text{g/L}$ , 5  $\mu\text{g/L}$ , 10  $\mu\text{g/L}$ , 25  $\mu\text{g/L}$ , 50  $\mu\text{g/L}$ , 75  $\mu\text{g/L}$ , and 100  $\mu\text{g/L}$  fluoride). Figure 2 shows an example chromatogram used for calibrating the instrument, and Figure 3 represents a calibration function for fluoride.

The AOF limit of detection (LOD) was 1.3  $\mu\text{g/L}$ , and the AOF limit of quantitation (LOQ) was 2.0  $\mu\text{g/L}$ . These values were calculated according to DIN 38402-60.<sup>27</sup>

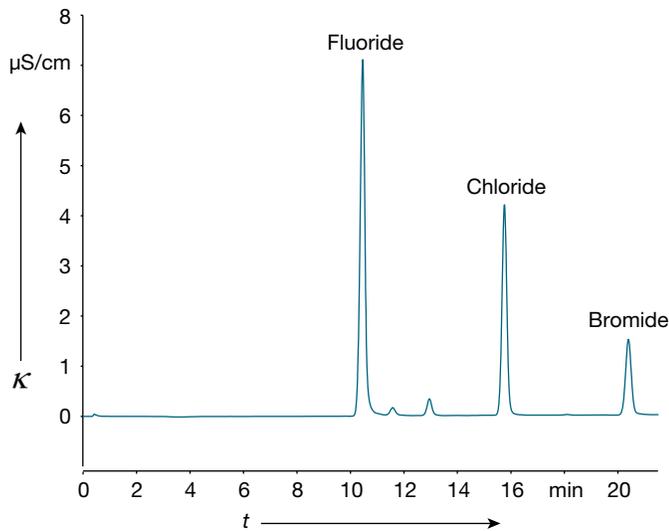


Figure 2. Standard chromatogram for the determination of organic adsorbable halogens (fluoride, chloride, and bromide, 100  $\mu\text{g/L}$  each)

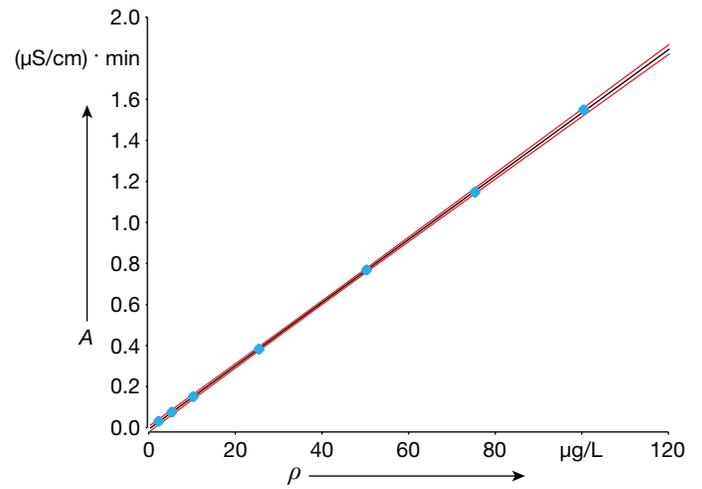


Figure 3. Calibration function for fluoride. Calibration range: 2–100  $\mu\text{g/L}$ . Confidence Intervals (red): Upper and lower probability of 99.5%.

### Presence of inorganic fluoride

Wagner *et al.* reported that inorganic fluoride present in a water sample at concentrations of less than 0.2 mg/L did not influence the AOF determination.<sup>28</sup> Wastewater samples with a higher level of inorganic fluoride, however, could be a critical matrix. Following this, von Abercron *et al.*<sup>22</sup> systematically studied the impact of higher concentrations of inorganic fluoride up to 50 mg/L, the maximum permissible value, according to the German wastewater ordinance.<sup>11</sup> The results showed that levels below 0.2 mg/L did not influence the AOF determination, while concentrations above 0.5  $\mu\text{g/L}$  of inorganic fluoride increased the AOF values. Consequently, all samples evaluated in this study were analyzed for inorganic fluoride before adsorption and combustion. All environmental samples showed concentrations for inorganic fluoride  $\leq 0.1$  mg/L, excluding any influence on the AOF results.<sup>22</sup>

Table 2. Fluoride calibration data; calibrated range 2  $\mu\text{g/L}$  to 100  $\mu\text{g/L}$

Peak name	Calibration	Levels	RSD	Coefficient of determination $r^2$ (%)	Offset	Slope
Fluoride	Linear, with offset	7	1.46	99.99	-0.0189	0.0164

RSD: Relative standard deviation in %

## Recovery studies

### Matrix-free solutions

Twenty-one fluorinated compounds or compound mixes and four industrial products served as model compounds. Ten perfluorinated alkyl compounds were selected according to DIN 38407-42<sup>4</sup>, and other PFAS and fluorinated compounds, as well as firefighting foam products, were also included. The chemical information and corresponding analytical data are summarized in

Table 3. Recovery ranged from 16% to 121%; the activated carbon did not retain the perfluorinated C1 and C3 carboxylic and sulfonic acids. The firefighting foam products showed recoveries in a range between 64% and 121%. The proportion of fluorine was calculated according to information provided by the respective manufacturer. As industrial products, their composition varies, which could explain the high recovery for one of the products.

**Table 3. Recoveries of fluorinated compounds and technical products from a DI water matrix after adsorption on activated carbon and CIC**

Group	Standard substance	Abbreviation	CAS No.	n	AOF (µg/L) measured value	AOF (µg/L) assigned value	RSD	Rec
Perfluoroalkyl-carboxylic acids (PFCAs)	Trifluoroacetic acid	TFA	76-05-1	3	<2	100	n.a.	<2
	Pentafluoropropionic acid	PFFPA	422-64-0	3	<2	100	n.a.	<2
	Perfluorobutanoic acid	PFBA	375-22-4	3	5.2	10	0.2	52
	Perfluoropentanoic acid	PFPeA	2706-90-3	3	9.5	10	0.2	95
	Perfluorohexanoic acid	PFHxA	307-24-4	3	8.4	10	0.1	84
	Perfluoroheptanoic acid	PFHpA	375-85-9	3	8.2	10	0.2	82
	Perfluorooctanoic acid	PFOA	335-67-1	5	6.4	10	0.9	64
	Perfluorononanoic acid	PFNA	375-95-1	3	4.7	10	0.6	47
	Perfluorodecanoic acid	PFDA	335-76-2	3	4.1	10	1.1	41
Perfluoroalkane-sulfonic acids (PFSA)	Trifluoromethanesulfonic acid	TMSA	1493-13-6	3	<2	100	n.a.	<2
	Perfluorobutanesulfonic acid	PFBS	29420-49-3	6	10	10	1.1	100
	Perfluorohexane sulfonic acid	PFHxS	355-46-4	3	9.4	10	1.7	94
	Perfluorooctane sulfonic acid	PFOS	56773-42-3	2	6.4	10	0.7	64
n:2 Fluorotelomer sulfonic acids (n:2 FTSA)	6:2-fluorotelomer sulfonic acid	H4PFOS	27619-97-3	5	8.9	14	0.3	63
PFAS mix	Mixture of PFCAs (C4-C10) and PFSA (C4, C6, C8)	Chiron AS	n.a.	4	8.6	13	0.4	66
				3	20	33	0.1	63
Perfluoroalkane sulfonates (PFSA)	Sodium perfluoro-1-pentanesulfonate	PFPS	n.a.	2	9.2	10	0.0	91
	Sodium perfluoro-1-propanesulfonate	PFPrS	n.a.	2	8.4	8.5	0.7	99
Polyfluoroalkyl ether carboxylic acids	2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	HFPO-DA	n.a.	2	11	13	0.0	87
Perfluoroalkane sulfonyl fluorides (PASFs)	Perfluoro-1-butanefluoride	PBSF	375-72-4	2	17	106	1.6	16
	Perfluoro-1-octanesulfonyl fluoride	POSF	307-35-7	2	24	94	1.5	26
Non-PFAS fluorinated compounds	4-fluorobenzoic acid	4-FBA	C7H5FO2	3	9.4	10	0.9	94
Firefighting foam fluorosurfactants (commercial products)	Product A	n.a.	n.a.	3	16	24	0.4	67
	Product A1	n.a.	n.a.	3	16	25	0.4	64
	Concentrate Product B	n.a.	n.a.	2	49	72	1.3	68
	Premix Product B	n.a.	n.a.	2	60	49	3.2	121

n: number of replicates

n.a.: not available

Rec: recovery in %

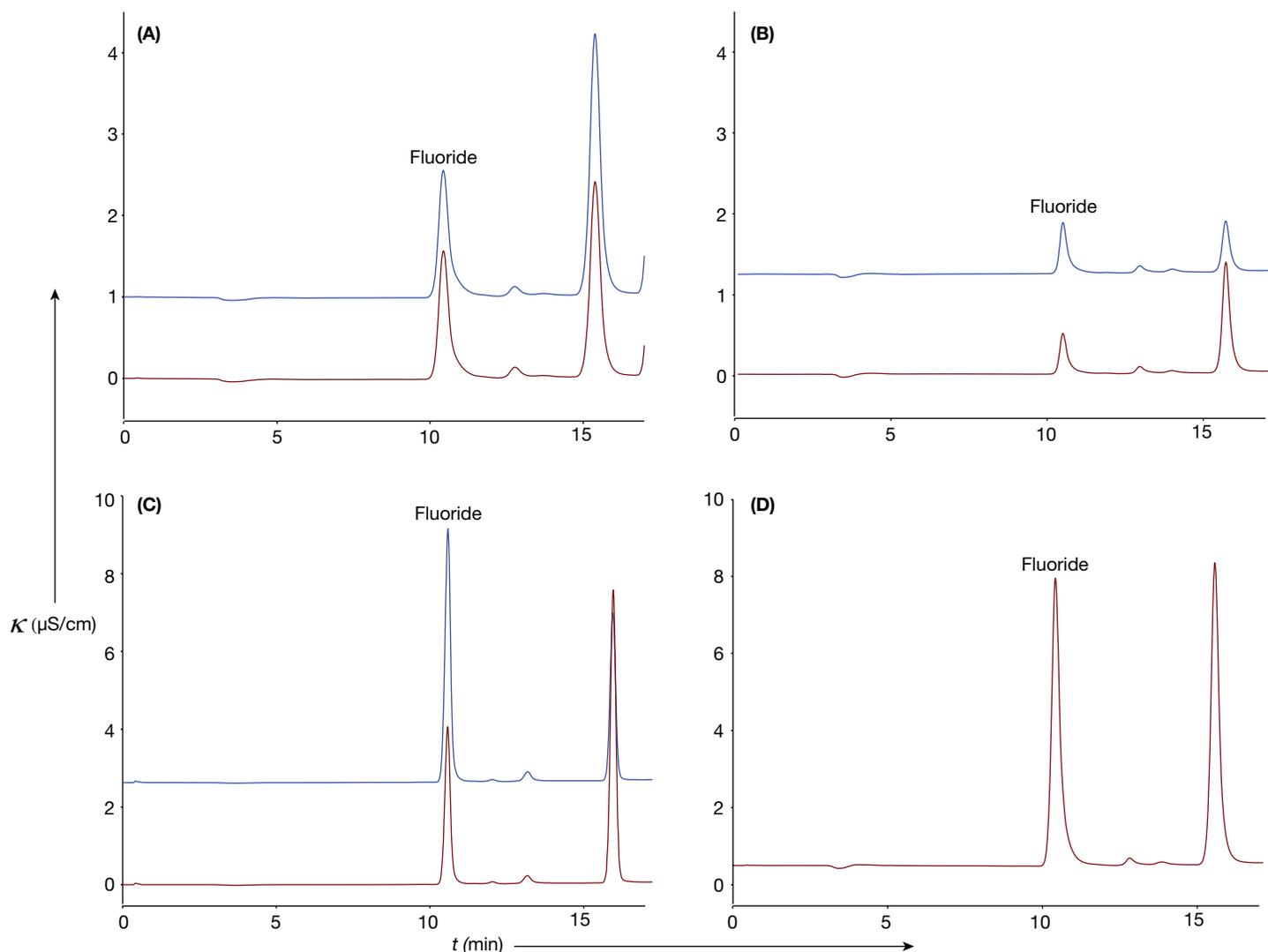
## Recoveries of PFBS and 4-fluorobenzoic acid in environmental water samples

PFBS was added to seven municipal wastewater and eight surface water samples to a final concentration of 10 µg/L AOF to test the recoveries of organic fluorinated compounds in environmental matrices. The wastewater matrix showed recoveries from 85% to 102%, while the surface water samples had AOF recoveries between 92% and 109%. The analytical recovery for 4-fluorobenzoic acid (4-FBA) in the municipal wastewater samples at a spiked concentration of 10 µg/L AOF ranged between 82% and 127% (Table 4). Willach *et al.* reported mean AOF recoveries from 51% to 100% for selected non-PFAS compounds (fluorinated pharmaceuticals and herbicides) in surface, ground, waste, and drinking water.<sup>29</sup>

Figure 4 shows a selection of example chromatograms obtained after combusting samples of different types and origins. The same analytical column setup was used throughout the two years of this study.

**Table 4. Recovery data for PFBS and 4-FBA**

Surface water		Wastewater		
Sample	PFBS recovery	Sample	PFBS recovery	4-FBA recovery
1	94	1	102	90
2	105	2	91	83
3	99	3	86	82
4	92	4	89	n.d.
5	109	5	93	n.d.
6	98	6	85	83
7	98	7	94	127
8	99			



**Figure 4. Selection of representative chromatograms obtained after adsorption on activated carbon and combustion. (A) municipal wastewaters, (B) groundwaters, (C) surface waters, (D) industrial wastewater (diluted 1 to 10)**

## Surface water

Samples from seven main rivers in Hesse, Germany, were investigated. Each sampling site was assessed up to 14 times between 2015 and 2017. In all cases, the AOF values were above the LOQ. During the measuring period of this study, the highest AOF value found was 24.5 µg/L, with an average between 4.5 and 10.2 µg/L AOF depending on the river and sampling period.

## Groundwater samples

Almost 100 groundwater samples from sites without reported risk of contamination with fluorinated compounds were analyzed for AOF and inorganic fluoride. In 60% of all cases, the results were below the LOD, while the remaining showed AOF-values between 2 and 7 µg/L. In all samples, inorganic fluoride was measured – excluding false-positive contribution to the AOF. Groundwaters showing elevated AOF values were subjected to a high performance liquid chromatography mass spectrometry (HPLC-MS/MS) analysis, according to DIN 38407-42.<sup>4</sup> Their PFAS values were between 0.1 and 0.4 µg/L, expressed as fluoride, which attested to the benefit of the parametric AOF-determination by CIC.

## Wastewater samples

### Municipal sewage treatment plants

A total of 116 discharge water samples from municipal sewage treatment plants were analyzed for AOF during the period of this study. For most of the samples (85%), the values were between 2 and 8.5 µg/L AOF. The rest showed values below the LOQ, and for one example, it was lower than the LOD. Even though the wastewater facilities served communities of different populations—from below 1000 to more than 100,000—the average AOF values were similar ( $3.4 \pm 0.2$  µg/L). It is interesting to note that the rivers to which the water treatment plants were connected showed AOF values ranging from 2.3 to 25 µg/L, which indicated other contributing sources.<sup>30-34</sup>

### Industrial wastewater

Eleven industrial wastewater samples from different locations were evaluated for AOF, resulting in values between < LOD to 19 µg/L. The treated wastewater discharge of a separate chemical plant was sampled over a year (n = 22), resulting in values above 74 µg/L, with a highest value of more than 500 µg/L. These samples were tested for the target fourteen PFAS according to DIN 38407-42 using HPLC MS/MS.<sup>4</sup> The sum of these fourteen PFAS amounted to a maximum of 5% of the reported AOF values, supporting the assumption that unidentified fluorinated samples are in the samples.

## Conclusion

The described AOF approach extends the analytical toolset to determine PFAS in environmental samples, such as surface water, groundwater, and wastewater. While LC-MS/MS and gas chromatography tandem mass spectrometry (GC-MS/MS)-methods use a specified set of PFAS for the evaluation, the adsorption process for the AOF method ensures the extraction and determination of more components—PFAS and other fluorinated compounds—than the previously mentioned approaches.

AOF determinations result in higher concentrations of PFAS—expressed as fluoride—compared to the highly selective LC-MS/MS approach. This indicates that the AOF procedure covers fluoroorganic compounds that are not readily determined by LC-MS/MS. The AOF levels found in surface water were higher than those of associated municipal sewage treatment plant discharges, supporting the theory of other sources contributing to the PFAS contamination of environmental samples.

The AOF-CIC-method, as a complement to existing approaches, provides an easy-to-use and economically attractive way to generate a cumulative parameter, and can help to optimize the utilization of the more expensive LC-MS/MS and GC-MS/MS instrumentation by selecting and only analyzing “suspicious” samples.

Note: This customer application note contains essential parts of Eleonora von Abercron’s doctoral thesis.

Thermo Fisher Scientific Notes: Today we would use a Thermo Scientific Dionex Integrion RFIC system for this work and a Dionex ADRS 2 mm suppressor.

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