Challenge
AOF determination requires the combustion of the enriched activated carbon under pyrohydrolytic conditions and thus a special digestion system with a water dosing unit.

Solution
ICprep ensures complete conversion of all organic fluorine compounds. The pyrohydrolytic system ensures a controlled supply of water during the combustion process.

Intended audience
Industrial (waste)water labs, monitoring authorities for environmental protection and nature conservation, contract labs for environmental analysis

Sample Digestion for AOF Determination According to EPA Method 1621

Introduction

Perfluorinated and polyfluorinated alkyl substances - PFAS for short - are not only present in our everyday products but are now also ubiquitous in our environment. The toxicity of individual substances for living organisms has been proven and individual chemical bans are active. PFAS are regarded as so-called forever chemicals, as they are only broken down very slowly and incompletely in the nature. They therefore constantly accumulate in water, soil, organisms and thus in our food chain. Due to the huge diversity of the substances, the unknown extent of their spread and their harmful effects on humans and the environment, monitoring is urgently needed. On the one hand, the analytical methods required for this must be able to detect the smallest quantities; on the other hand, the diversity of individual compounds (> 4700 registered substances) makes it difficult to fully record all representatives. In addition to an already established single substance analysis for a manageable selection of perfluorinated carbonic and sulfonic acids using chromatographic mass spectrometric methods (HPLC-MS, HPLC-MS/MS), the need for a simple and reliable screening parameter is increasing. The determination of the sum parameter AOF is ideal for this purpose. The parameter AOF - adsorbable organically bound fluorine - represents perfluorinated and polyfluorinated alkyl substances as well as other organic fluorine compounds such as pharmaceuticals and pesticides.

The determination of AOF is now described in various standard methods, including EPA 1621[1]. The determination is based on the enrichment of organic fluorine compounds on activated carbon columns as first step, followed by combustion of the loaded columns at ≥ 1000 °C in a pure oxygen or oxygen-argon atmosphere with the addition of water (pyrohydrolysis) and adsorption of the formed HF gas in aqueous solution. In the last step the fluorine content of this solution is detected using ion chromatography. Combustion and detection can take place in a so-called CIC system or in two separate devices (pyrohydrolytic combustion + IC). This means that all furnaces/high-temperature combustion systems that allow controlled water dosing during combustion and enable the absorption of the sample gases in an aqueous solution can be used for AOF sample preparation. For example, AOX analyzers specially upgraded for pyrohydrolysis or the ICprep system described in this paper. The separation of digestion and detection increases the application flexibility and utilization of existing systems. The AOF measurements presented below were performed with an ICprep and an independently operated ion chromatograph to demonstrate the suitability of the digestion system for the determination of AOF according to EPA method 1621[1].

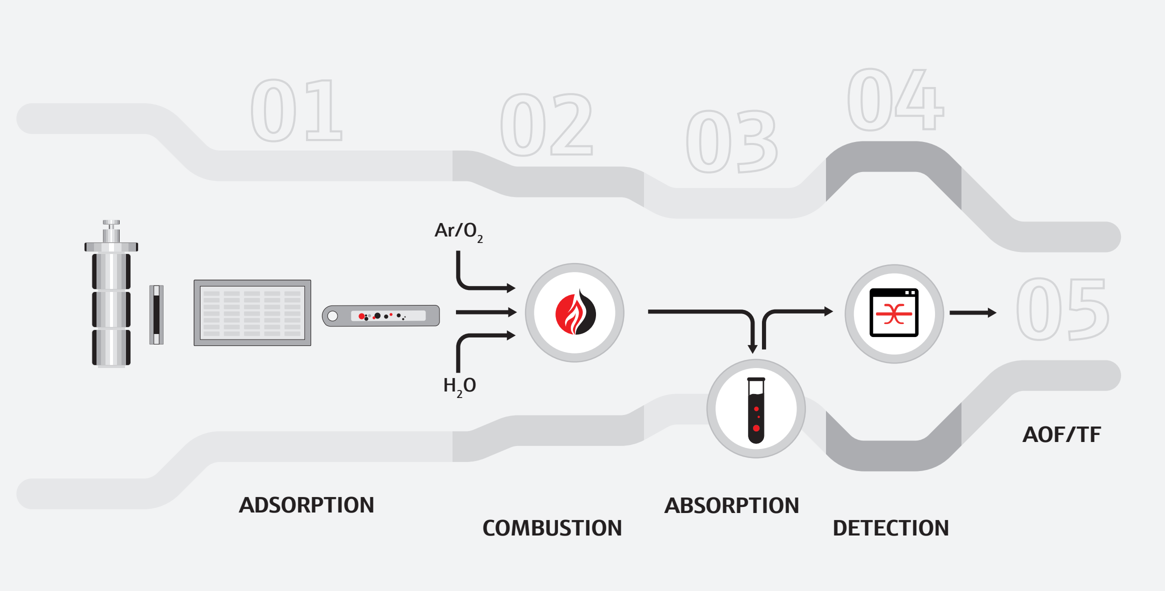

Figure 1: Complete AOF analysis workflow (ICprep is used for the step of sample digestion according to pyrohydrolysis)

Materials and Methods

Three systems were used to determine the AOF in aqueous standards and water samples:

- AOF column adsorption unit type APU sim for the adsorption of the analytes on activated carbon columns
- Pyrohydrolytic high-temperature combustion system type ICprep automatic for the digestion of the loaded activated carbon columns and the absorption of the reaction gas (HF) in the integrated fraction collector
- Detection unit, ion chromatograph, with conductivity detector for fluoride ions

Thanks to the separation of combustion (ICprep) and detection (IC), the respective process steps could be carried out flexibly in terms of time without waiting or downtimes.

Samples and reagents

- PFAS standard solution: potassium salt of perfluorohexane sulfonic acid (PFHxS) with 25 µg/L AOF
- Two water samples: wastewater and surface water

Sample preparation

The organic fluorine compounds were enriched using the column method in accordance with EPA 1621. The samples for the AOF determination were first prepared by adding 0.5 mL $NaNO_3$ stock solution (2 mol/L $NaNO_3$) to 100 mL of the unacidified original samples. The samples were then adsorbed onto special, low-blank AOF activated carbon columns using the APU sim. The washing process to remove inorganic fluorine compounds was then carried out automatically with 25 mL of a 0.01 mol/L $NaNO_3$ wash solution.

Further information on the enrichment of activated carbon can be found in the application note “Sample preparation for the determination of AOF in water according to DIN 38409-59”.

Instrument and method settings

The appropriately prepared activated carbon columns were placed on the sample tray of the ICprep automatic and automatically fed into the combustion furnace. The sample combustion took place in a two-stage process: In the first stage, the volatile sample components were vaporized in an argon stream, followed by the combustion of the gaseous products formed in an oxygen-rich atmosphere. In the second process phase, all remaining sample components were quantitatively mineralized in pure oxygen and converted to HF. Here, the integrated flame sensor ensured safe and complete combustion. The flame sensor eliminates the need for time-consuming method development and the creation of sample feed parameters, and its advantages are particularly useful for more complex solid and liquid samples. During the entire combustion process, a high-resolution syringe pump ensured a defined and constant water dosage. The gaseous analyte HF was absorbed in an aqueous solution. This solution was transferred and collected into a vessel (15 mL centrifuge tube) of the integrated fraction collector using a syringe pump. Integrated rinsing processes ensured complete transfer of the analytes and carry-over-free work.

Table 1: Settings on ICprep automatic

Parameter	Setting
Furnace temperature	1050 °C
O_2 main flow (main)	300 mL/min
Ar flow (inlet)	150 mL/min
O_2 flow (inlet)	150 mL/min
Post-combustion time	300 s
Water dosage	0.2 mL/min
Absorber supply	2 mL
Post-purge volume	1 mL

Results and Discussion

As part of these investigations, an initial test of the ICprep system was carried out in accordance with EPA method 1621, in order to demonstrate its basic suitability and performance. For this purpose, the so-called method blank value as well as the recovery and precision of a PFAS standard solution (PFHxS) with 25 µg/L AOF were analyzed. First, 100 mL of ultrapure water and 100 mL of the PFAS standard solution were enriched on activated carbon, then digested in the ICprep and analyzed using an IC.
The results of the initial performance test (IPR) are summarized in Table 2.

Table 2: Results of the initial performance and recovery test (IPIR)

Sample ID	Meas. 1 [µg/L]	Meas. 2 [µg/L]	Meas. 3 [µg/L]	Meas. 4 [µg/L]	Mean value [µg/L]	Recovery [%]	RSD [%]
Method blank	0.98	0.75	0.63	0.70	0.76	-	20
PFAS standard 25 µg/L AOF	23.7	23.5	23.6	23.8	23.6	95	0.5

The EPA method specifies the following criteria for the initial suitability test of the system: the recovery rate for the PFAS standard should be within 80% to 120%, the relative standard deviation (RSD) from four determinations should be ≤ 20%. Table 2 illustrates that both requirements are easily met by the ICprep system and subsequent detection. According to EPA method 1621, the method blank value should not exceed a level of 4 µg/L; the average method blank value achieved is far below this requirement at 0.76 µg/L AOF.
The analytical results of the surface waters tested and a water sample spiked with PFHxS are summarized in Table 3.

Table 3: Results of AOF determination

Sample ID	**AOF [µg/L], measurement 1**	**AOF [µg/L], measurement 2**	**AOF [µg/L], mean value**	**SD [µg/L]**	**Recovery rate [%]**
Method blank	1.10	0.86	0.98	0.17	-
Standard solution with 25 µg/L AOF (QC resp. OPR)	23.3	23.1	23.2	0.14	93
Wastewater	7.43	8.09	7.76	0.47	-
Surface water	1.68	1.90	1.79	0.16	-
Matrix spikes (MS + MSD) (spiked surface water: 50 mL sample + 50 mL PFAS standard c = 25 µg/L AOF)	12.5	12.6	12.6	0.07	86 RPD = 0.8%

EPA 1621[1] specifies the following measurement sequence for a working day:

a) First, at least two empty sample boats should be "burned"
b) Determination of the method blank value by analyzing the activated carbon columns after enrichment of ultrapure water and rinsing with nitrate wash solution
c) Control measurement of a PFAS standard (Ongoing Precision and Recovery "OPR") by analyzing the activated carbon columns after enrichment of a PFHxS-solution in the medium concentration range of the calibration (IC) and rinsing with nitrate wash solution
d) Analysis of ten or fewer samples in the form of loaded and rinsed activated carbon columns
e) Analysis of samples spiked with PFHxS (so-called matrix spike "MS" and a duplicate "MSD")

In addition, the calibration of the ion chromatograph is checked at the beginning and end of each measurement sequence using inorganic standard solutions (NaF).

The following criteria apply to the quality control of the overall system:
The method blank value should not exceed 4 µg/L AOF, although this is not a binding requirement and higher blank values can be used if necessary. As can be seen from the measurement data, reproducible blank values of around 1 µg/L AOF can be achieved with the aid of the ICprep system and subsequent detection, which is particularly advantageous for the analysis of less contaminated water samples. A recovery rate in the range of 70% to 130% is required for the ongoing testing of the precision and recovery of the PFHxS standard (OPR). Here too, the measured values of > 90% prove the basic suitability of the ICprep as a digestion system. Furthermore, spiked samples, so-called matrix spikes, are analyzed as part of the precision and accuracy check. The surface water spiked with PFHxS provided a very good recovery of 86%; the EPA method requires a recovery rate of 50% to 150% at this point. Another quality criterion is the relative percentage difference between the recoveries of the two spiked samples "MS" and "MSD", which should be ≤ 30%. For the spiked samples measured, this difference was < 1%.
Overall, all measurement results prove that the ICprep digestion system can be used to lay the foundation for reliable and reproducible AOF results.

Summary

Figure 2: ICprep automatic with APU sim

Digestion for AOF determination in accordance with EPA method 1621[1] can be carried out in a time and cost-efficient manner using the ICprep. Particularly for smaller sample volumes, which do not yet justify the purchase of an expensive coupled CIC (combustion-ion chromatography) system, a separate pyrohydrolytic digestion system can be a cost-effective alternative, provided that an existing ion chromatograph is utilized to a higher degree. Even with regard to the determination of very low AOF concentrations and the achievement of low blank values, separate systems have no disadvantage compared to coupled systems (CIC), as evidenced by the measured values.
In addition to the ICprep, the described digestion can also be carried out with an AOX analyzer multi X 2500 or an elemental analyzer multi EA 5X00, if these are equipped with a corresponding kit for pyrohydrolysis and absorption. In this way, these analyzers can also be used for AOF determination, thereby increasing capacity utilization. The use of a ceramic combustion tube is possible too.

Recommended device configuration

Table 4.1: Overview of required devices, accessories and consumables – fully automated solution

Article	Article number	Description
APU sim	450-900.300	Sample preparation system for the determination of AOF, AOCl, AOBr, AOI and AOX according to column method
ICprep automatic	450-300.102	Flexible system for sample digestion using pyrohydrolytic high-temperature combustion
Solids kit for MMS	450-300.034	MMS accessory for automated dosing of solids
Boat sensor	450-889.204	Sensor for MMS for additional safety when analyzing saline samples
multiWin software	450-011.803	Control software
Set of 100 disposable columns for AOF 18 x 6 mm, filled	402-880.616	Set of 100 AOF columns 18 x 6 mm, filled

Table 4.2: Overview of required devices, accessories and consumables – extension of a present analysis system

Article	Article number	Description
APU sim	450-900.300	Sample preparation system for the determination of AOF, AOCl, AOBr, AOI and AOX by column method
Extension kit ICprep basic	450-300.110 or	Kit for expanding a multi X 2500 or multi EA 5X00 for sample preparation for solid, liquid, EOF and AOF samples after pyrohydrolytic high-temperature combustion, absorption and collection of the reaction gases formed for further analysis steps
Extension kit ICprep automatic	450-300.111	Inclusive automatic collection of absorption solutions by fraction collector
multiWin 5 - Upgrade to current version	450-011.804	Upgrade of existing multiWin 5 version to enable utilization of ICprep functions
Activated carbon columns for AOF determination, 18 x 6 mm	402-880.616	Set of 100 AOF columns 18 x 6 mm, filled

References

[1] EPA Method 1621, January 2024: „Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)"

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