Challenge
AOF determination requires the combustion of the loaded 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 combustion system provides a controlled supply of water for digestion.

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

Sample digestion for AOF determination in accordance with DIN 38409-59 and ISO 18127

Introduction

The parameter AOF – adsorbable organically bound fluorine – represents fluorinated pharmaceuticals and pesticides as well as the large group of per- and polyfluorinated alkyl substances (PFAS). PFAS are now omnipresent in our environment. They are persistent and cannot be recorded as individual substances in their entirety, due to their large number and diversity, which makes environmental monitoring difficult. This is where a sum parameter such as AOF can make a valuable contribution as a screening parameter. The determination of AOF in water samples (wastewater, surface water, groundwater, etc.) thus provides important decision-making aids for further investigations in PFAS single substance analysis.

In sum parameter analysis, it is always necessary to define specific, standardized conditions under which the determination procedure is carried out. The framework for the determination of the convention parameter AOF is provided by DIN 38409 part 59 and ISO 18127. The method for AOF determination is based on the enrichment of organic fluorine compounds on activated carbon (adsorption step), followed by combustion at ≥ 950 °C in an oxygen atmosphere with the addition of water (pyrohydrolysis) (digestion step). The detection of the fluoride ions formed is carried out using ion chromatography. Combustion and detection can be carried out either directly afterwards requiring a coupled system including all components (on-line), or separately in two separate devices (off-line). This means that all furnaces/high-temperature digestion systems that allow controlled water dosing during combustion and enable the absorption of the formed reaction gases in an aqueous solution can be used for AOF sample digestion. 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, utilization of any existing systems,

while increasing the throughput speed for both separated steps.
The methods according to DIN 38409-59 and ISO 18127 are applicable from an AOF concentration of ≥ 2 µg/L. A missing or insufficient amount of water during combustion can lead to an underestimation of the AOF. The AOF measurements presented below were carried out with an ICprep and an independently operated ion chromatograph, in order to demonstrate the suitability of the digestion system for the determination of AOF in accordance with the standard.

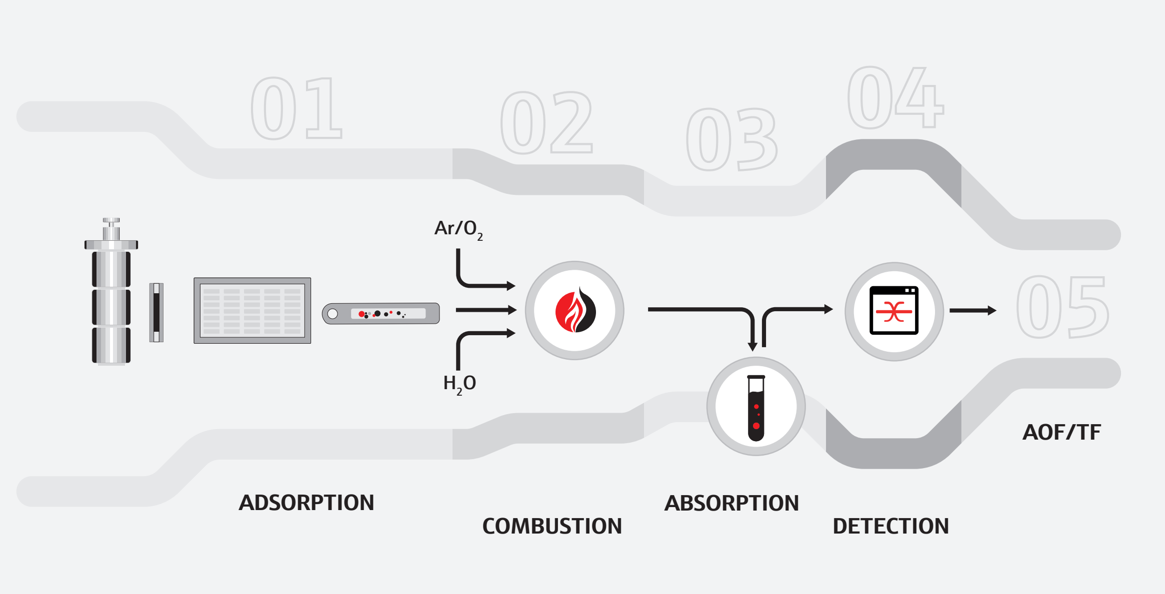

Figure 1: Complete AOF analysis workflow (ICprep is used for the step of sample digestion according to pyrohydrolysis)

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

- Standard solutions AOF (4-fluorobenzoic acid in ultrapure water) with 5, 10, 25, 50 and 100 µg/L AOF
- Three water samples: two surface waters and one wastewater

Sample preparation

The organic fluorine compounds were adsorbed on activated charcoal using the column method in accordance with DIN 38409-59 and ISO 18127. 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 on 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 and ISO 18127”.

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 inert gas 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 first carried out in accordance with DIN 38409-59 and ISO 18127, in order to demonstrate its suitability in principle. For this purpose, five AOF control solutions with AOF concentrations of 5 µg/L, 10 µg/L, 25 µg/L, 50 µg/L and 100 µg/L were enriched on activated carbon, subsequently incinerated in the ICprep and analyzed using an IC system.
The results of the initial test are summarized in Table 2 and represent the mean value from three individual measurements of the concentration level investigated.

Table 2: Results of the initial test

Sample ID	Mean value AOF [µg/L], (blank corrected)	RSD [%]
AOF standard 5 µg/L	4.7	2.4
AOF standard 10 µg/L	9.5	3.4
AOF standard 25 µg/L	24	4.4
AOF standard 50 µg/L	50	6.5
AOF standard 100 µg/L	107	2.9

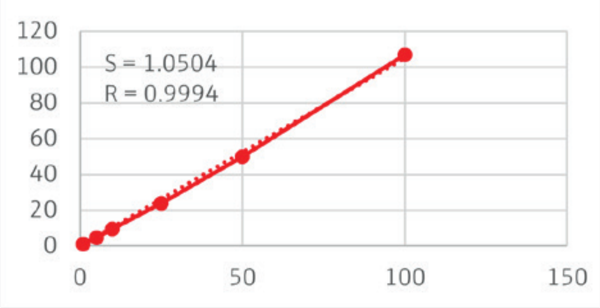

Figure 2: Graphical illustration of the initial test

The DIN 38409-59 and ISO 18127 standards specify the following criteria for the initial testing of the system: a slope (S) of 0.9 to 1.1 should be achieved and the correlation coefficient (R) should be ≥ 0.99. Figure 2 illustrates that both requirements are met by the ICprep system and the subsequent detection. Looking at the relative standard deviations (RSD) for the individual concentration levels, which were each calculated from three individual measured values, these are, with one slight exception, well below 5%.
The analysis results of all samples tested 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], measurement 3	AOF [µg/L], mean value	SD [µg/L]
Blank	1.1	0.69	0.67	0.82	0.24
Surface water 1	1.4	1.6	1.1	1.4	0.25
Surface water 2	1.7	1.9	2.3	2.0	0.30
Wastewater	7.5	8.1	7.4	7.7	0.38
Control standard 5 µg/L AOF	4.9	4.6	4.6	4.7	0.17

Blank values should be determined every working day at the start of a series of measurements. The standard method DIN 38409-59 does not stipulate any specific requirements here, but notes that AOF blank values in the range of 1 µg/L can be achieved in practice. This statement can be confirmed with the mean blank value of 0.82 µg/L obtained here. It should also be noted that the contribution of the device blank value to the blank value of the overall procedure is generally negligible. The materials used for sample enrichment (activated carbon) make a significant contribution to the process blank value. For the daily analysis of an AOF control solution within the expected concentration range of the samples, DIN 38409-59 and ISO 18127 state that the AOF value obtained and the theoretical value below 20 µg/L may not differ by more than 2 µg/L. The measured AOF value of the 5 µg/L control solution was 4.7 µg/L and therefore fulfills this criterion.
According to the standard, analysis results are usable if their difference is not more than 2 µg/L in the range below 20 µg/L AOF. All measured sample values meet this requirement. The standard deviations (SD) achieved for the concentration range below 20 µg/L AOF are very low.
Overall, all the measurement results prove that the ICprep digestion system can be used as the basis for reliable and reproducible AOF results.

Summary

Digestion for AOF determination in accordance with DIN 38409-59[1] and ISO 18127[2] can be carried out in a time and cost-efficient manner using the ICprep. Particularly for smaller sample numbers, which do not yet justify the purchase of an expensive coupled CIC (combustion-ion chromatography) system, separate pyrohydrolytic digestion 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 obtained.
In addition to the ICprep, the described digestion can also be carried out with an AOX analyzer type multi X 2500 or an elemental analyzer type 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 sample preparation, thereby increasing capacity utilization.

Figure 3: ICprep automatic with APU sim

Of course, an ICprep system can also be used to digest prepared water samples for the determination of AOCl, AOBr or AOI in accordance with DIN 38409-59 and ISO 18127. It is also possible to use a ceramic combustion tube.

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
Solid 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] DIN 38409-59, Oktober 2022, „Bestimmung von adsorbierbarem organisch gebundenem Fluor, Chlor, Brom und Iod (AOF, AOCl, AOBr, AOI) mittels Verbrennung und nachfolgender ionenchromatographischer Messung (H 59)“

[2] ISO 18127:2026, Water quality — Determination of adsorbable organically bound fluorine, chlorine, bromine and iodine (AOF, AOCl, AOBr, AOI) — Method using combustion and subsequent ion chromatographic measurement

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