Challenge

Can sample preparation for the determination of AOF be performed with an AOX sample preparation system?

Solution

Samples for AOF determination can be prepared quickly and easily with the semi-automated APU sample preparation system, which can also be used for AOX (AOCl, AOBr, and AOI) sample preparation.

Sample preparation for the determination of AOF in water samples in accordance with DIN 38409-59 and ISO 18127

Introduction

The term "adsorbable organically bound fluorine" (AOF) covers all organic fluorine compounds, including above all perfluorinated and polyfluorinated alkyl substances (PFAS). These can be determined as a sum parameter according to a defined procedure. The substance group of PFAS now comprises more than 4,700 substances[1] that are present in many everyday products and give them special properties. Their water-, dirt- and oil-repellent effects are used, for example, in the manufacturing of textiles and food packaging. PFAS are also found in foam extinguishing agents, pesticides, medicines, ski waxes, and other lubricants, as well as many other consumer goods.
PFAS are non-aromatic organic molecules whose hydrogen atoms are completely or partially replaced by fluorine atoms. All these persistent substances are only degraded very slowly and incompletely by natural means and therefore constantly accumulate in the environment (water, soil, organisms, food chain). For some representatives of the PFAS, toxicity to humans has been proven a very low levels and recommendations exist in this regard from the European Food Safety Agency for a maximum weekly intake by humans.[1] PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanesulfonic acid) are the best known representatives of PFAS. Both are classified and regulated as POPs (persistent organic pollutants) in the Stockholm Convention with the aim of a worldwide ban on their use. At the European level, this applies to several other representatives of PFAS.[1] Due to the diversity of the substances and the still unknown extent of their distribution and effects on humans and the environment, monitoring is urgently needed.
On the one hand, the analytical methods required for this purpose must be able to detect the smallest quantities; on the other hand, the variety of individual compounds makes it difficult to completely record all representatives. In addition to an already established single compound

analysis for only a selection of perfluorinated carboxylic and sulfonic acids via chromatographic mass spectrometric methods (HPLC-MS, HPLC-MS/MS), the importance of an inexpensive and reliable screening parameter is increasing. The determination of the sum parameter AOF is suitable for this purpose. AOF can be used for the monitoring of water quality. Its determination is based on the definition of relevant conditions under which organically bound fluorine adsorbs on activated carbon and is subsequently detected. The method thus represents an analytical convention. The range of application covers all waters, from low-polluted groundwaters to wastewaters of all kinds. If waters containing particles are analyzed, the AOF bound to the particles is also detected. The AOF determination method is based on the enrichment of fluoroorganic compounds on activated carbon and their subsequent combustion at temperatures ≥ 950 °C in an oxygen-containing gas stream with the addition of water (= hydropyrolysis). In this process, organic fluorine compounds are converted to hydrogen fluoride (HF), which is first absorbed in aqueous solution and detected as fluoride by means of ion chromatographic measurement. Parallel to AOF determination, AOCl, AOBr, and AOI can also be determined using this method. The method is also known as combustion ion chromatography (CIC). Direct coupling of the combustion system with the ion chromatograph can prove advantageous for the determination of trace contents; an offline variant is often also practicable.

After sampling, sample pretreatment and enrichment, has a significant influence on the quality of the analytical results. Here, some specifics are to be considered for AOF.

Figure 1: APUsim sample preparation system

Materials and Methods

In contrast to sample pretreatment for AOX analysis according to DIN EN ISO 9562[2], samples for AOF determination are not acidified with HNO_3 to pH < 2 during or immediately after their collection. Therefore, their storage time in the refrigerator is also limited to 5 days; frozen (-18 °C) samples can be stored for up to 4 weeks. It is recommended to analyze samples quickly after collection. Glass bottles are best suited as sampling vessels. If the sample is to be frozen first, then plastic bottles made of fluorine-free material (e.g., PP, PE) are used. The vessels must always be completely filled.

Sodium sulfite addition, which is usually practiced for AOX determination in the presence of active chlorine, is unnecessary for AOF.

The first process step for the determination of AOF is the enrichment on activated carbon. The column method is preferred for this. In case of very high particle load of the sample or homogenization is not possible, the shaking method (batch method) can also be used.

Reagents

- Activated carbon columns for AOF analysis (iodine number > 1050 mg/g)
- Nitrate stock solution for AOF analysis (2 M $NaNO_3$)
- Nitrate washing solution for AOF analysis (0.01 M $NaNO_3$)
- Ultrapure water as blank solution
- 4-fluorobenzoic acid solutions to check the overall procedure (concentrations typically between 5 µg/L and 100 µg/L

Sample preparation and measurement

The analysis sample for the AOF determination is prepared by adding 0.5 mL $NaNO_3$ stock solution to 100 mL original sample. If the sample has to be diluted, not less than 5 mL of the original sample should be used for this purpose. Subsequently, the analytical samples are adsorbed on activated carbon using a suitable apparatus. According to DIN 38409-59[3] and ISO 18127[4], a pump should be used for this process step. The analysis sample is passed over activated carbon columns arranged vertically in series. The APUsim sample preparation unit, which is described below, can be used for this purpose.

Up to 6 samples can be processed simultaneously with the APUsim. For this purpose, 3 independently controllable channels are available, each of which can process 2 samples in parallel. The sample volume, rinsing volume, and flow rate can be varied. The activated carbon columns can have different dimensions (diameter, length).

The homogenized samples are drawn up into fluorine-free plastic syringes (max. volume 100 mL) which are inserted into the upper part of the apparatus. Alternatively, an empty plastic syringe can be placed on top first and then filled with

the sample. This method is recommended for samples with a very high particle load. Here, rinsing with nitrate wash solution should then also be carried out by filling the rinsing solution into the syringes, in order to rinse any particles that may have adhered, onto the activated charcoal columns.
The activated charcoal tubes are inserted into appropriate column holders (duplex column, triplex column, or similar) and then attached to a Lure connector in the central part of the apparatus. Here, the use of a variety of column dimensions from a wide range of manufacturers is possible. The number of columns used can also be varied. The drainage channel is then pushed upwards to ensure splash-free dripping during the adsorption and rinsing process.
The storage bottle for the rinsing solution is now filled with nitrate wash solution for the AOF determination, placed on the right side of the apparatus and the hose inserted accordingly.
The enrichment and rinsing parameters are now set via the operating menu. It is important here that the set sample volume (maximum 100 mL) and the actual sample volume in the syringe match. The enrichment or rinsing flow rate can be variably adjusted in the range from 1 mL/min to 6 mL/min, as can the rinsing volume from 0 mL to a maximum of 100 mL. The settings apply to one of the three available channels in each case. The start button (located centrally below the syringes) now starts the automatic processing (enrichment + rinsing) for one sample channel at a time.

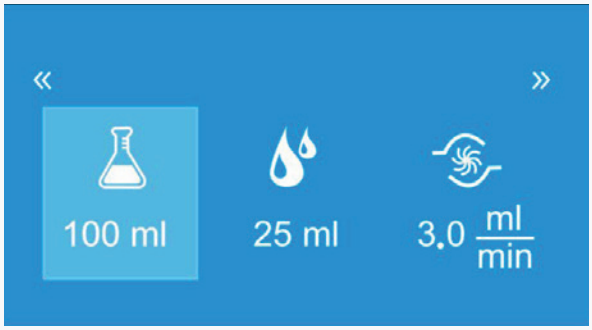

Figure 2: APUsim operating menu

Table 1: Method settings for AOF sample preparation

Parameter	APUsim
Sample volume	100 mL
Adsorption flow rate	3 mL/min
Rinsing volume	25 mL
Rinsing flow rate	3 mL/min

Comparison of sample preparation methods AOF and AOX

Table 2: Comparison of sample preparation steps and parameters AOF and AOX

Parameter	AOF according to DIN 38409-59 / ISO 18127	AOX according to DIN EN ISO 9562
Sampling	In glass bottles or halogen-free plastic bottles completely filled (PP, PE)	In glass bottles or plastic bottles (e.g., PTFE)
Acidification with HNO_3	None	With HNO_3 conc., at least 2 mL to 1 L sample, pH < 2
Sodium sulfite addition	None	10 mL 1 M Na_2SO_3 to 1 L sample if active chlorine/ oxidizing agent is suspected in the sample
Addition of $NaNO_3$ stock solution	0.5 mL 2 M $NaNO_3$ stock solution to 100 mL sample. Attention: Stock solution is neutral, does not contain HNO_3!	5 mL 0.2 M $NaNO_3$ stock solution to 100 mL sample. Attention: Stock solution is HNO_3 -acidic!
Sample volume for enrichment	100 mL	100 mL
Activated carbon amount	At least 50 mg	Each column about 50 mg
Number of columns	2 or more columns, pre-columns for retention of particles permissible	2 columns
Adsorption apparatus	Suitable pump, halogen-free tubing, sample introduction from the top of the columns	Suitable pump, hoses for example made of PTFE
Adsorption and washing flow rate	3 ± 0.1 mL/min	3 mL/min

Table 2 (continued): Comparison of sample preparation steps and parameters AOF and AOX

Parameter	AOF according to DIN 38409-59 / ISO 18127	AOX according to DIN EN ISO 9562
Wash volume ($NaNO_3$ wash solution)	25 mL 0.01 M $NaNO_3$ wash solution (without HNO_3)	25 mL 0.01 M $NaNO_3$ wash solution (with HNO_3)
Requirements blank value overall procedure	< 5 µg/L	< 30 µg/L
Treatment in the presence of inorganic halides	Fluoride can contribute to the AOF and must therefore be determined in the sample. If necessary a matrix blank value must be determined and taken into account, or the use of the SPE-AOF method must be considered (Annex F of DIN 38409-59).	For chloride > 1g/L dilution is recommended or the application of the SPE-AOX method (Annex A of DIN EN ISO 9562).

The parameters relevant for the setting on the APUsim sample preparation system are underlined in the table above. It is obvious that the setting parameters for the AOF sample preparation are identical to the parameters for the AOX determination. The only difference is the sodium nitrate wash solution used, which is prepared from the nitric acid-free stock solution for the AOF determination. Thus, by simply replacing this solution, the APUsim can be used both for preparing samples for AOF determination and for enriching and rinsing samples for AOX determination. For this purpose, only the corresponding rinsing solution is placed in the APUsim and a rinsing process with 10 mL rinsing volume is started. After about 3 minutes, all sample-carrying components (hoses, valves) are free of residues of the previously used wash solution. It is of course also possible to use the sample preparation unit for the determination of AOCl, AOBr, and AOI according to DIN 38409-59 and ISO 18127. This is carried out analogously to the AOX preparation according to DIN EN ISO 9562.

Conclusion

With the APUsim automatic sample preparation unit, up to 6 samples can be automatically prepared for AOF determination within less than 45 minutes. The system is characterized by the use of fluoride-free materials for all components that come into contact with the sample. The contribution of the APUsim to the total blank value of the AOF procedure is thus negligible.

All types of aqueous samples can be processed. For samples with a high particle load, a so-called pre-column can be used in addition to the activated carbon columns, which safely retains the particles and is later analyzed together with the charcoal columns. The user is also flexible in the choice of activated carbon columns used in terms of their dimensions and number. A quick change from sample preparation for AOF determination to AOX sample preparation is possible at any time.

In addition, the preparation system offers the convenient option of preparing water samples using the SPE method as well. This again applies to the SPE-AOF as well as to the SPE-AOX or -AOCl, -AOBr and -AOI determination.

The sample throughput for AOF/AOX analysis can be drastically increased with several APUsim devices working in parallel. As an alternative to the simultaneous enrichment of samples, sequentially operating APU 28 enrichment systems are also available, which are mainly used in overnight operation. The APUsim is ideally suited for all types of sample preparation for the determination of adsorbable organically bound halogens.

Overview of devices and consumables

Table 2: Overview of devices and consumables

Article	Article number	Description
APU sim	450-900.300	Sample preparation system for the determination of AOF, AOCl, AOBr, AOI, and AOX, as well as for their SPE variants by column method
Activated carbon columns for AOF, 18 mm x 6 mm	402-880.616	Set of 100 disposable tubes for AOF 16 x 8 mm, filled
Activated carbon columns for AOF/ AOX, 40 mm x 9 mm	402-880.620	Set of 100 disposable tubes for AOF/AOX 40 x 9 mm, filled
Activated carbon columns for AOX, 18 mm x 6 mm	402-880.610 402-880.615	Set of 100 disposable tubes for AOX 18 x 6 mm, filled Set of 300 disposable tubes for AOX 18 x 6 mm, filled

References

[1] Bund für Umwelt und Naturschutz Deutschland e.V. (BUND), Friends of the Earth Germany, „Fluorchemikalien: Langlebig, gefährlich, vermeidbar", Berlin, Oktober 2021

[2] DIN EN ISO 9562:2005-02 Water quality - Determination of adsorbable organically bound halogens (AOX)

[3] DIN 38409-59:2020-11 - Draft: Determination of adsorbable organically bound fluorine, chlorine, bromine and iodine (AOF, AOCl, AOBr, AOI) using combustion and subsequent ion chromatographic measurement (H 59)

[4] ISO 18127:2026-02, 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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