Challenge
Fast screening of PFAS in soil and sewage sludge

Solution
Simple, fast, and cost-effective sum parameter method EOF - extraction of fluorinated organic compounds and detection by molecular absorption spectrometry (MAS) using contrAA 800

Intended audience
Governmental and private research centers and institutes in the field of environmental analysis, contract laboratories, wastewater treatment plants

Determination of PFAS in Soil and Sewage Sludge as a Sum Parameter EOF (Extractable Organically Bound Fluorine)

Introduction

PFAS are per- and polyfluoroalkylated substances with persistent properties, which have therefore been and still are used in everyday objects (e.g., water-repellent coatings for textiles and paper, cookware). Due to their multiple uses, PFAS are currently found in numerous environmental samples. Besides monitoring of surface water or contaminated soils, control at wastewater treatment plants is of increasing interest.
Since PFAS are very resistant to conventional biological treatment in wastewater plants, they can not be removed from wastewater without a special treatment step and are therefore often found in the effluent of wastewater treatment plants or in sewage sludge. Furthermore, during the biological treatment process in the wastewater treatment plant, other unknown per- and polyfluorinated substances can be formed from polyfluoroalkyl precursor compounds in addition to the persistent perfluoroalkyl acids (PFAA, such as PFOS and PFOA).
The determination of individual substances is, on one hand, expensive and very time-consuming, on the other, does not work for unknown compounds. A fast and easily detectable sum parameter for fluorinated organic compounds would help to detect an increased load in the sewage plant promptly and to prevent the entry of PFAS-polluted wastewater into the environment. For soil-related use, sewage sludge in Germany is not permitted to contain more than 100 µg/kg PFAS[1].
Extractable organic fluorine compounds (EOF) can be quantitatively detected by extraction followed by molecular absorption spectrometry (MAS) detection. MAS is based on the detection of fluorine via the *in situ* formation of gallium (I) fluoride (GaF) molecules, which are detected by the contrAA 800, a high-resolution graphite furnace AAS with a continuum light source. A particular advantage is the very low detection limit of this method. Due to its detection strength, the EOF offers a good alternative and extended application possibility to the parameter AOF - the adsorbable organically bound fluorine in aqueous environmental samples.

Material and Methods

Samples

- 2 sewage sludge samples (dried and milled)
- NCS DC 73325 reference soil

Reagents

- HNO_3 (65%)
- 0,05 % TritonX-100
- Pd/Mg/Zr modifier (1 g/L Pd, 0.5 g/L Mg, 0.02 g/L Zr)
- Ca modifier (ICP standard, 1 g/L)
- Ga solution (ICP standard, 1 g/L)
- Sodium acetate (per analysis)
- Zr stock solution (ICP standard in HCl, 1 g/L)
- Certificated F stock solution (1.000 g/L F ICP standard as NaF)
- Methanol (for LC)
- Acetone (100%)
- Acetic acid (100%)
- 4-fluorobenzoic acid (98%)
- Nonafluorobutane-1-sulfonic acid (PFBS)
- lomefloxacin hydrochloride (LF)

Sample preparation – extraction

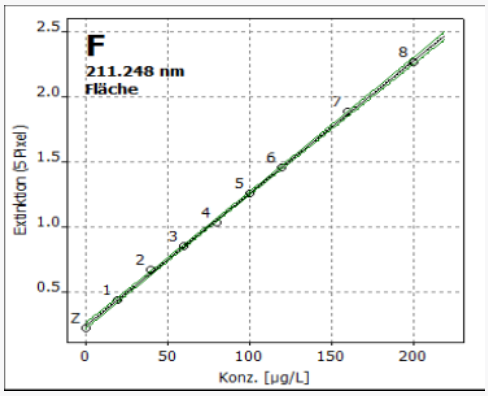
The sample extracts were prepared as following: a sample amount of ca. 1 g was suspended in 5 mL of acetic acid-methanol mixture, sonicated for 10 minutes, and then centrifuged. After the supernatant was transferred into a fresh falcon tube, the residue was again resuspended in 5 mL of fresh extraction solution and the extraction step was repeated. After the transfer of the second supernatant, the extraction was repeated for a third time. All three supernatants obtained from one sample portion were merged and dried completely under a gentle argon flow. The dried extract was than solved in 2 mL of methanol-water mixture 1:1 (v/v), again ultrasonicated and undiluted residues were removed by centrifugation.

Table 1: Sample preparation

Parameter	Specification
Sample weight	ca. 1 g
Extraction solution	5 mL of 0.5% acetic acid in methanol
Ultrasound bath, extraction step	10 min
Centrifugation, extraction step	10 min at 4,500 rcf
Repetition of the extraction step	3 times
Extract drying	Complete evaporation under Ar stream
Resuspension solution	2 mL of methanol-water mixture 1:1 (v:v)

Calibration

The calibration standards were prepared by autosampler dilution of premixed anorganic F stock solutions (100 µg/L and 200 µg/L) in 0.5% HNO_3 (subboiled). Table 2 shows the concentrations of the calibration standards. The calibration curve is shown in figure 1. Based on the calibration curve and the measured blank values, a detection limit of 2.386 µg/L fluorine was calculated for the MAS method.



Calibration function: linear
$R^2_{adj} = 0.9999$

Figure 1: Calibration curve of F as GaF-Molecule)

Table 2: Concentration of the calibration standards (made of: * 100 µg/L or ** 200 µg/L F stock solutions)

Standard	Concentration of the stock solution [µg/L]	Volume of stock solution [µL]	Analyte concentration [µg/L]
Cal. std. 0	-	0	0
Cal. std. 1	100	4*	20
Cal. std. 2	100	8*	40
Cal. std. 3	100	12*	60
Cal. std. 4	100	16*	80
Cal. std. 5	100	20*	100
Cal. std. 6	200	12**	120
Cal. std. 7	200	16**	160
Cal. std. 8	200	20**	200

Instrumentation

The contrAA 800 (G/D) with graphite furnace technique and the autosampler AS-GF, jointly controlled by the ASpect CS software, were used for the determination of fluorine. At first, graphite tubes were coated with zirconium (35 µL stock solution, six times) and afterwards conditioned using calcium solution (25 µL of 20 mg/L Ca solution) and Pd/Mg/Zr modifier (15 µL).
Fluorine is determined by reacting with the gallium solution and measuring the molecular absorption band of gallium monofluoride (GaF) at 211.248 nm. Each sample was analyzed three times.

Table 3: Instrument specifications

Parameter	Spezifikation
Device	contrAA800 G/D
Tube type	PIN platform
Autosampler	AS-GF
Injected volume	4-20 µL (standards), 20 µL (sample)
Rinsing solution	2% HNO_3, 0.05% TritonX-100

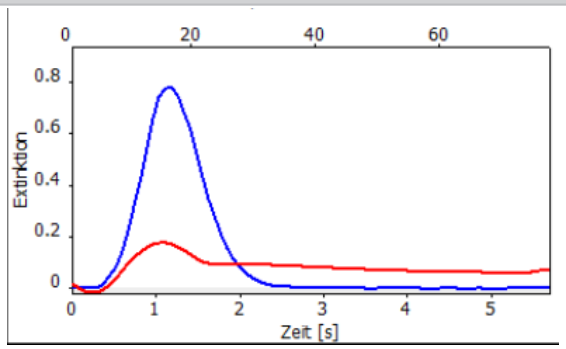
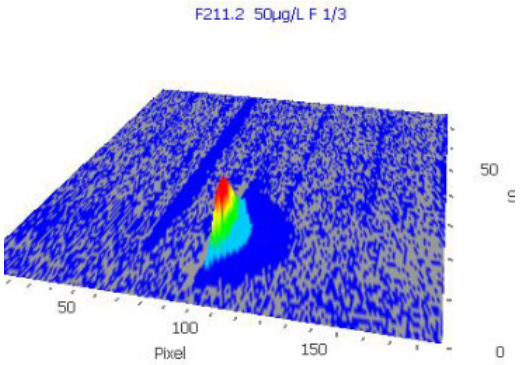
Table 4: Method settings and evaluation parameters

Wavelength [nm]	Number of evaluation pixels	Measuring time [s]	Modifier	Reagent	Baseline correction
211.248	5	6	3 µL Pd/Mg/Zr	9 µL Ga solution	IBC

Table 5: Furnace program for the detection of GaF molecules

Step	Name	Temp (°C)	Ramp (°C/s)	Hold (s)	Gas purge
1	Drying	65	4	5	Max.
2	Drying	80	5	25	Max.
3	Drying	90	5	20	Max.
4	Drying	110	5	10	Max.
5	Pyrolysis	700	50	10	Max.
6	Gas adaption	700	0	5	Stop
7	Atomize	1500	1500	6	Stop
8	Clean	2450	500	5	Max.

Table 6: Characteristic signal shape and spectral vicinity of the analyte line

Element	Signal profile	3D spectrum
F		

blue: analyte signal, red: background signal

Results and Discussion

The EOF value was determined using the established method in 3 different sludge and soil samples. Each measurement was repeated three times. The obtained values and RSDs together with calculated original sample concentrations are listed in the Table 7.

Table 7: Detection of EOF in different sludge and soil samples

Sample	Sample weight [mg]	Measured value [µg/L]	Sample concentration [µg/kg]
Sludge 1	1337.8	68.2	102.0
Sludge 2	1098.9	49.1	89.4
NCS DC 73325	1005.3	6.28	18.8

These results have a good correlation with the concentration range. For similar samples known from literature[2].
In order to examine the reliability of the established method, the resulting reproducibility of the complete procedure was determined. For this purpose, the extraction step followed by the fluorine detection were repeated independently six times for the sample sludge 2. The obtained data is presented in Table 8. A low RSD value (6 of 6) of 2.14% was able to be achieved.

Table 8: Reproducibility of the complete method (extraction and detection)

Sample	Sample weight [mg]	Measured value [µg/L]	Sample concentration [µg/kg]
Sludge 2_1	1007.4	44.2	87.9
Sludge 2_2	1010.3	43.8	86.7
Sludge 2_3	1300.1	57.6	88.6
Sludge 2_4	1278.0	58.3	91.3
Sludge 2_5	998.7	46.1	92.3
Sludge 2_6	999.0	44.7	89.5
Sludge 2_average	1098.9	49.1	89.4 ± 1.91 (2.14%)

The accuracy of the current method was checked by adding (spiking) a known amount of fluorinated organic substances direct to the sample extracts, as no reference material of organically bound fluorine is available.
As is already known from the literature[3] and shown at the determination of fluorine in surface water samples[4], the recovery of spikes increases with the thermal stability of the added substance. The recovery rates of the individual substances such as 4-fluorobenzoic acid (4-FBA) and nonafluorobutane-1-sulfonic acid (PFBS) with lower thermal stability (with boiling point 4-FBA: 253.687 °C and PFBS: 210-212 °C) was not satisfactory. When lomefloxacin (with a boiling point of 542.7 °C) was added to the mixture a good recovery rate of 90.2% was found. For this purpose, 3 substances were used: 4-fluorobenzoic acid (4-FBA), nonafluorobutane-1-sulfonic acid (PFBS) and lomefloxacin (LF). The data is shown in the Table 9.

Table 9: Recovery rate of organic fluorine spikes in sample sludge 2

Spike substance	Boiling point	Spike concentration [µg/L]	Measured value without spike [µg/L]	Measured value with spike [µg/L]	Recovery [%]
LF	542.7 °C	51.58	44.26	90.80	90.2

Summary

The quantification of PFAS in different solid samples as a sum parameter can be carried out very quickly and easily with the described EOF method using the contrAA 800. The applied sample preparation is commonly used for the analysis of solid samples such as sludges, soils, and sewage sludges. Also the analysis of other solid materials, like fibers and textiles, is conceivable. The detection method of fluorine in the extracts by means of the molecular absorption of the *in situ* formed gallium monofluoride with the contrAA 800 is fully automatable and highly efficient in detection. The results of the EOF measurements for sewage sludge are significantly higher compared to the EOF value for soil. The reproducibility was checked by one sample and is very good at about 2%. The recovery of an organic fluorine compound was determined up to 90%. In addition to single-substance analysis, the EOF determination with the contrAA 800 is a useful screening method for fluorinated organic compounds. The results can be determined relatively quickly and thus allow a faster action posibilities.
Unknown compounds, which can be formed by chemical degradation or conversion processes could be recorded. For the evaluation of a concrete effected toxicity of PFAS on humans, animals, and nature, it is recommended to additionally analyze of the individual substances.

Figure 2: contrAA 800 D with AS-GF autosampler

Recommended device configuration

Table 10: Overview of devices, accessories, and consumables

Article	Article number	Description
contrAA 800 G	815-08001-2	High-resolution continuum source AAS (HR-CS AAS) for graphite furnace technique
AS-GF autosampler	–	Included in the system
Chiller	–	Included in the system
Consumable set G	810-60066-0	Consumable set for graphite furnace technique novAA / contrAA

References

[1] German federal environment agency: The magazine of the German federal environment agency 1/2020 Focus PFAS – Came to stay, Publication as PDF: https://www.umweltbundesamt.de/publikationen/schwerpunkt-1-2020-PFAS

[2] Simon, F.; Gehrenkemper, L.; von der Au, M.; Wittwer, Ph.; Roesch, Ph.; Pfeifer, J.; Cossmer, A. and Meermann B. A fast and simple PFAS extraction method utilizing HR–CS–GFMAS for soil samples. Chemosphere. 2022, 295, 133922

[3] Metzger, M.; Ley, P.; Sturm, M. and Meermann, B.: Screening method for extractable organically bound fluorine (EOF) in river water samples by means of high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CD GFMAS9, Anal. Bioanal. Chem. 2019 Jul; 411 (19): 4647-4660

[4] Analytik Jena application note: Determination of extractable organically bound fluorine (EOF) in surface waters by molecular absorption spectrometry, 12/2020

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