Challenge
A sum parameter for the determination of EOF in surface water.

Solution
Determination of extractable organically bound fluorine (EOF) in surface water with molecular absorption spectrometry.

Determination of Extractable Organically Bound Fluorine (EOF) in Surface Water With Molecular Absorption Spectrometry

Introduction

A wide range of materials based on fluorinated organic compounds with highly desirable properties has been created during the last decades and their amount is constantly growing. The chemical resistance and physical properties of fluorinated organic substances are used in many everyday products and applications, from pharmaceuticals through fine and specialty chemicals to polymers(1). The consequence of the accelerating production of fluorinated organic substances is their increased occurrence in the environment. Some of these substances are already listed as persistent organic pollutants by the Stockholm Convention (Annex B -restriction) and the European water framework directive (WFD).
Besides the known substances further toxic fluorine species can occur due to decomposition or microbial degradation. The determination of single compounds is time-consuming and cost-intensive. Therefore, a sensitive screening method of fluorinated organic compounds as sum parameter enables a fast monitoring of the environmental pollution. The presented method of the quantitative determination of extractable organically bound fluorine (EOF) as sum parameter in surface waters, recently developed by the Federal Institute of for Materials Research and Testing, Germany(2), combines solid phase extraction (SPE) and molecular absorption spectrometry (MAS).
The SPE is suitable for multiple enrichment of organic compounds as well as separation of interfering inorganic fluoride. This procedure can be simplified by the sample preparation device APUsim, that offers the flow speed control and allows simultaneous handling of up to six samples. The contrAA 800 with its integrated Xenon short arc lamp and its high-resolution spectrometer offers low detection limits as well as the possibility to record molecular bands besides the atomic absorption. This allows the quantification of non-metals such as F via GaF molecular absorption(3,4).

Materials and Methods

Reagents

- HNO_3 (65%, per analysis)
- 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)

Samples

- Fluorinated organic substances: 4-fluorobenzoic acid, nonafluorobutane-1-sulfonic acid, lomefloxacin hydrochloride
- River water samples from the rivers Saale (in Jena), Saarbach (close to Gera), White Elster (in Gera)

Sample preparation

Solid phase extraction was performed on SPE cartridges (polystyrene-divinylbenzene absorbent resin) using APUsim sample preparation system. The cartridges were first conditioned with 10 mL methanol and rinsed with 100 mL acidified deionized water. After the required sample volume was pumped through the cartridge, it was rinsed again with 100 mL acidified deionized water and dried for about 20 minutes. Trapped organic substances were eluted with 5 mL methanol followed by
5 mL acidified deionized water. The resulting 10 mL methanol-water eluate was used directly for measurement of fluorine by MAS with the contrAA 800.

Table 1: Instrument specification APUsim

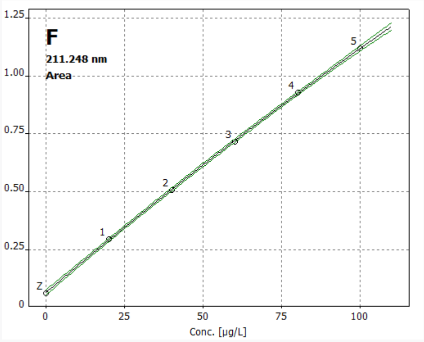
Parameter	Specification
Sample preparation device	APUsim
SPE cartridges	Chromafix HR-P (Macherey-Nagel)
Flow speed	3 mL/min (conditioning, elution), 5 mL/min (sample)
Sample volume	500–2,500 mL
Conditioning volume	10 mL methanol
Elution volume	5 mL methanol, 5 mL acidified water

Calibration

The calibration standards were prepared by autosampler dilution of a pre-mixed F stock solution (100 µg/L) in 0.5% HNO_3 (subboiled). Table 2 shows the concentrations of the calibration standards. The calibration curve is presented in Figure 1.

Table 2: Concentration of the calibration standards

Standard solution	Volume of stock solution [µL]	Analyte concentration F [µg/L]
Cal. std. 0	0	0
Cal. std. 1	4	20
Cal. std. 2	8	40
Cal. std. 3	12	60
Cal. std. 4	16	80
Cal. std. 5	20	100



non-linear rational
$R^2 = 0.9992$
LOQ = 0.115 mg/L

Figure 1: Calibration curve of F (as GaF molecule)

Based on the calibration curve and measured blank values, the LOD of 3.247 µg/L for the MAS fluorine detection method was calculated.

Instrumentation

The measurements for the determination of fluorine were carried out by the contrAA 800 with graphite furnace technique and AS-GF autosampler controlled by ASpect CS software. Thus, all reagent additions and analysis steps are fully automated.

The graphite tubes were first coated with zirconium (35 µL stock solution, 6 times) and afterwards conditioned using calcium solution (25 µL of 20 mg/L Ca solution) and Pd/Mg/Zr modifier (15 µL). To all standards and samples, 9 µL Ga stock solution were added to convert Fluorine stoichiometrically into gallium monofluoride (GaF). The molecular absorption bands of gallium monofluoride (GaF) was used to quantify the fluorine content in the prepared samples (eluate) and standards. Each eluate was analyzed three times.

Table 3: Instrument specifications

Parameter	Specification
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

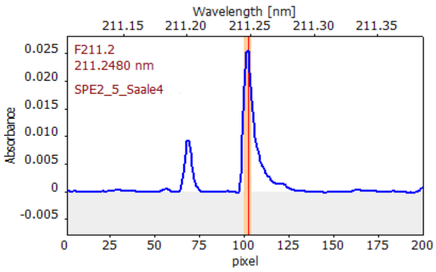
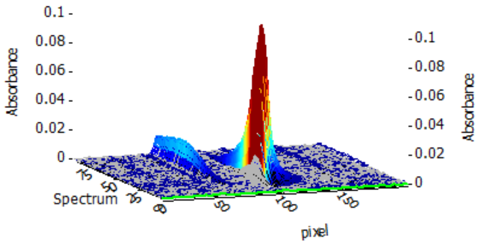
Table 4: Method settings and evaluation parameters

Molecule	Wave-length [nm]	No. of eval. pixels	Measuement time [s]	Modifier	Reagent	Baseline correction
GaF	211.248	5	6.5	3 µL Pd/Mg/Zr 3 µL NaAc solution	9 µL Ga solution	IBC

Table 5: Furnace program for detection of GaF molecule

Step	Name	Temperature [°C]	Ramp [°C/s]	Hold [s]	Gas purge
1	Drying	80	5	25	max
2	Drying	90	5	15	max
3	Drying	110	5	15	max
4	Pyrolysis	500	200	10	max
5	Gas adaption	500	0	5	stop
6	Atomize	1,600	1,500	6	stop
7	Clean	2,450	500	5	max

Table 6: Characteristic signal shape and 3D spectrum

Element	Signal profile *	3D spectrum
F (sample "Saale")		

Results and Discussion

Measurement of surface water samples

10 L river water from the rivers Saale (in Jena), White Elster (in Gera) and Saarbach (near Gera) were taken as samples several times between June and July 2020. The samples were acidified with HNO_3 and divided into 3 aliquotes. 2.5 L or 1.5 L from the samples were applied per one SPE cartridge (enrichment factor 250 and 150 resp.). The sample preparation was performed twice (2 cartridges) for each sample. The measurement results are shown in Table 7.

Table 7: Measurement results of surface water samples

Sample $_{\text{sampling date}}$	**Enrichment factor**	**Measured value [µg/L] F (as GaF)**	**RSD [%]**	**Sample concentration [ng/L]**
Saale $_{\text{June,30,2020}}$	250	42.59	2.9	170.4
Saale $_{\text{July,13,2020}}$	250	43.62	4.7	174.5
Saale $_{\text{July,15,2020}}$	150	24.04	3.6	160.2
White Elster $_{\text{Juli12,2020}}$	250	60.76	2.6	243.0
Saarbach $_{\text{Juli12,2020}}$	250	28.66	5.7	114.6

The determined concentrations of EOF in river water samples are comparable with previously published data for Rhine and Moselle, where the EOF concentrations were found to be between 50 and 300 ng/L (2).

Recovery rates for organic standards

The recovery rate of the SPE-MAS method was tested using three different substances: 4-fluorobenzoic acid (4-FBA), nonafluorobutane-1-sulfonic acid (PFBS), lomefloxacin hydrochloride (LF). The solutions with final concentration of 1 µg/L F (for lomefloxacin additional concentrations of 0.5 and 2 µg/L) were prepared using acidified deionized water. Each time 500 mL of solution was used per one extraction. Extraction steps were repeated twice resp. three times independently. Each eluate was measured 3 times by MAS. The results are summarized in the Table 8 and Figures 2 and 3.

Figure 2 shows that all different initial concentration of LF were found with very good recovery rates. The recovery rate for different fluorinated organic substances can vary depending on the substance properties, as shown in Figure 3. These results are consistent with the data available in publications which show a correlation between the melting point of the substance of interest and its recovery rate (2).

Table 8: Measurement results of test solutions of fluorinated organic substances

Sample (Eluate)	**Enrichment factor**	**Measured value [µg/L] F (as GaF)**	**RSD* [%]**	**Sample concentration [ng/L]**	**Sample target concentration [ng/L]**	**Recovery rate [%]**
4-FBA$_{avg}$	50	31.79	6.2	635.8	1,000	63.6
PFBS$_{avg}$	50	20.58	5.1	411.6	1,000	41.2
LF0.5$_{avg}$	50	24.19	3.8	483.9	500	96.8
LF1$_{avg}$	50	48.35	5.9	967.0	1,000	96.7
LF2$_{avg}$	50	110.9	1.2	2,219	2,000	110.9

* RSD for measurements of different eluates, 4- FBA, PFBS with 3 extraction eluates, LF with 2 extraction eluates

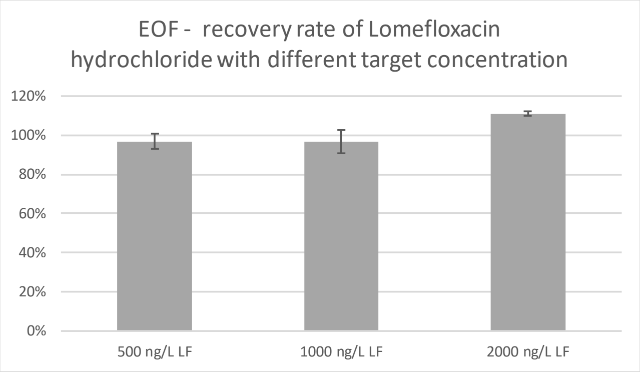


Figure 2: Influence of the initial concentration

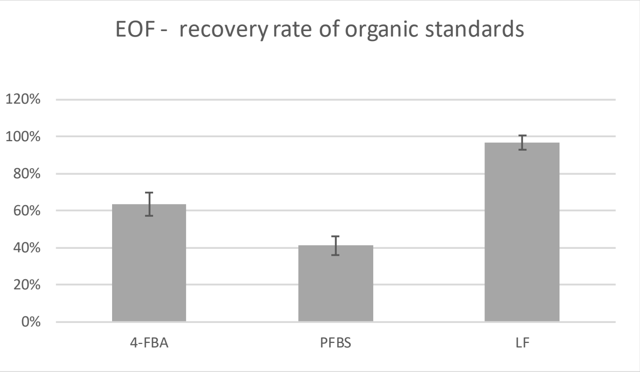


Figure 3: Detectability of different organic standards

Influence of inorganic fluorine

The influence of inorganic fluorine on the determination of organically bound fluorine was tested by adding a higher amount of inorganic F to the solution of fluorinated organic substance 4-FBA. The solutions of 4-FBA with a concentration of 1 µg/L F were prepared using acidified deionized water and spiked with NaF to the concentration of 100 µg/L and 1 mg/L inorganic F. For one extraction step 500 mL of each solution was used, resulting in an enrichment factor of 50. The extraction steps were repeated three times. The resulting eluates were measured three times by MAS. The results presented in Figure 4 show the same values for the determined EOF content of approximately 28 µg/L with and without inorganic fluorine matrix. Inorganic fluorine in the tested concentration range has no influence on the recovery rate of the organically bound fluorine and therefore on the results of EOF in the sample.

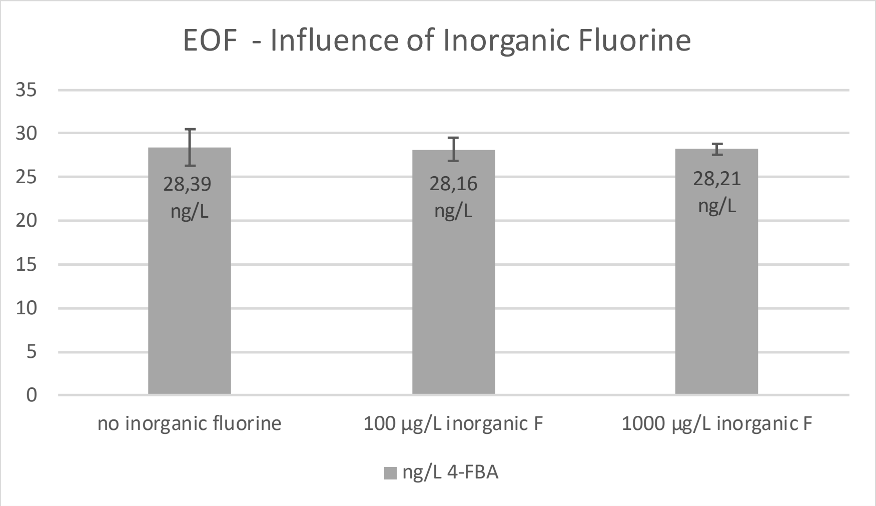


Figure 4: Influence of inorganic fluorine

Matrix effects

Native matrix effects on the determination of extractable organically bound fluorine were tested by spiking of river water sample with a known concentration of fluorinated organic substance (lomefloxacin 333 µg/L F). For one extraction 1.5 L of the solution was used. Extraction steps were repeated two times, independently from each other. The resulting eluates were measured three times by MAS. Two non-spiked samples (Saale control) were analyzed in the same way in parallel, to check the influence of the matrix. The obtained results are presented in the Table 9. The recovery rate of extractable organically bound fluorine in natural matrix was approximately 86%.

Table 9: Measurement results of water samples, spiked with lomefloxacin

Sample	Enrichtment factor	Measured value [ug/L] F^- (as GaF)	RSD [%]	Actual concentration in sample [ng/L]	Spike [ng/L]	Sample target concentration [ng/L]
$\text{Saale}_{\text{control}}$	150	23.09	4.37	153.9	0	-
Saale_LF	150	62.89	3.88	419.3	333.3	487.3

Summary

The described EOF method based on SPE and MAS presents a fast and sensitive method for the analysis of extractable organically bound fluorine in surface water samples.

This study shows that the SPE-MAS method can be successfully applied for EOF determination in natural water resources by using APUsim for the sample preparation and contrAA 800 graphite furnace technique for the detection. The results of the determination of extractable organically bound fluorine by MAS are very well reproducible.

In summary, the EOF as a sum parameter for fluorinated organic compounds is a reasonable screening method for environmental pollution. With the presented method increasing EOF concentrations can be detected quickly and cost-effective. Nevertheless, a detection of single substances is necessary to evaluate the concrete environmental impact of substances and their toxicity.

Figure 5: contrAA 800

References

[1] Richard, D., Chambers, F.R.S.: Fluorine in organic chemistry, Blackwell Publishing Ltd. 2004.

[2] 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

[3] U. Heitmann, H. Becker-Ross, S. Florek M.D. Huang, M. Okruss: Determination of non-metals via molecular absorption using high-resolution continuum source absorption spectrometry and graphite furnace atomization, J. Anal. At. Spectrom., 21 (2006) 1314–1320.

[4] H. Gleisner, B. Welz, J. W. Einax: Optimization of fluorine determination via the molecular absorption of gallium mono-fluoride in a graphite furnace using a high-resolution continuum spectrometer, Spectrochmicia Acta Part B 65 (2010) 864–869.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.4 · Author: OlWe/AnJu
en · 10/2025