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Sum parameter for PFAS

Sum parameter for organic fluorine compounds

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- **PFAS** are per- and polyfluoroalkylated substances with persistent properties
- Detectable in numerous environmental samples
- Increasing interest in monitoring in wastewater treatment plants

Utilization of Per- and Polyfluorinated Compounds (PFC)

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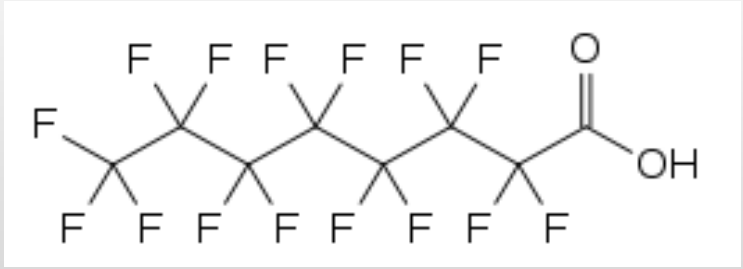
PFAS

Non - PFAS

Per- and Polyfluorinated Compounds (PFC)



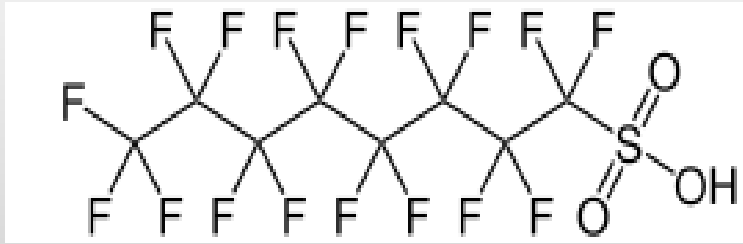
Perfluorooctanic acid (PFOA)

Properties of technical used compounds:

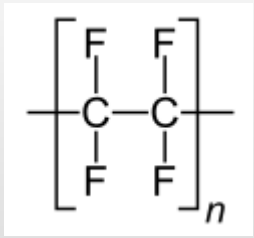
- Chemical resistant
- Thermal resistant
- UV – light resistant

Properties of pharmaceutical used compounds:

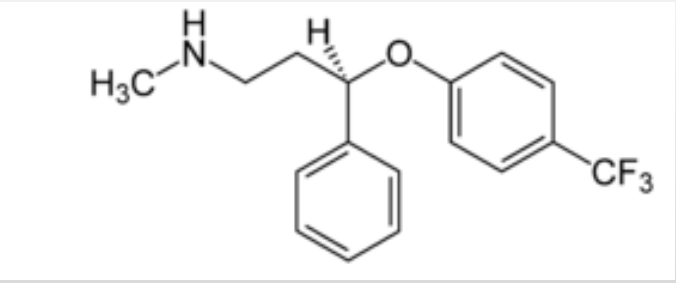
- Fat solubility
- Alternation with enzymes
- Slow metabolism



Perfluoroctanesulfonic acid (PFOS)



Polytetrafluoroethylen (PTFE)-Teflon



Fluoxetin - Antidepresiva

Per- and Polyfluorinated Compounds (PFC) in Environment

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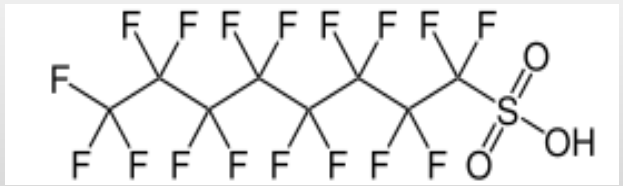
Risk assessment of fluorinated organic substances

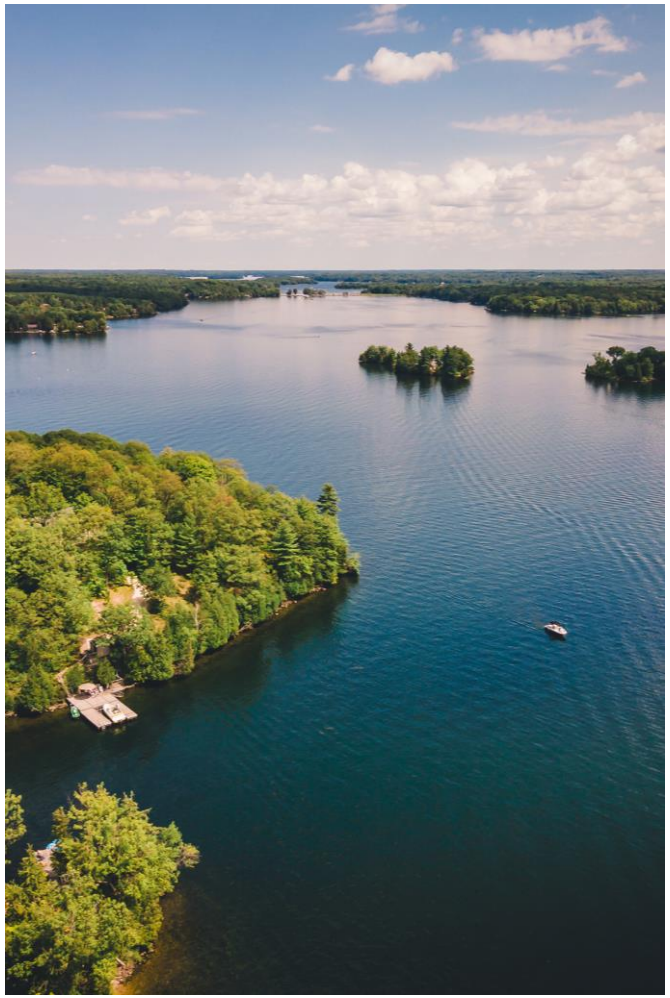
- Substances of Very High Concern (SVHC)
- Persistent
- Bio-accumulative
- Toxic
- Mobile
- Carcinogenic
- Toxic for reproduction



Perfluoroctanesulfonic acid (PFOS)

Water directive:
0.65 ng/L for inland surface water
0.13 ng/L for surface water

Tolerable weekly intake:
13 ng/kg body weight per week



Sum parameter for organic fluorine compounds

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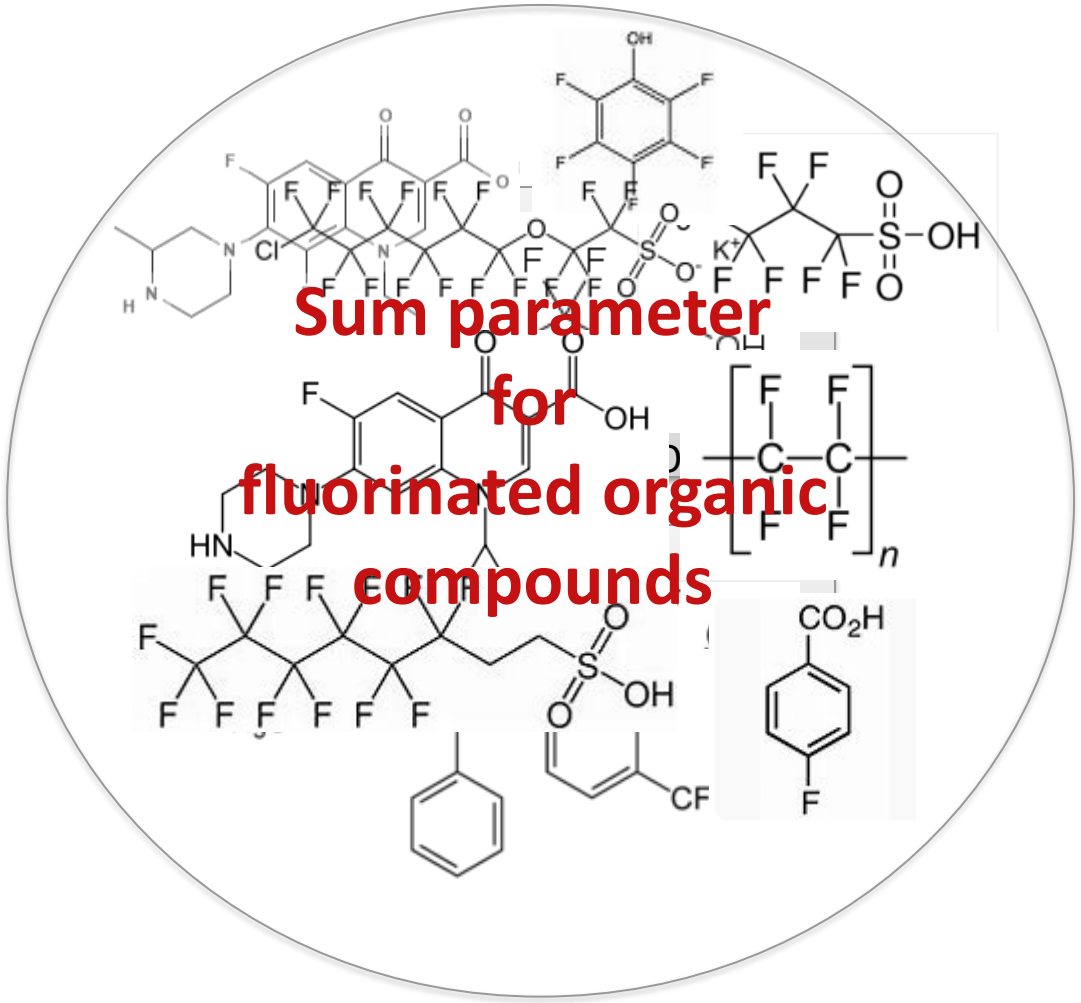
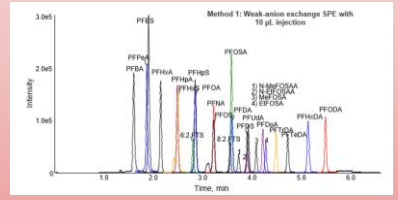
Analysis of a sum parameter



Method for single compounds

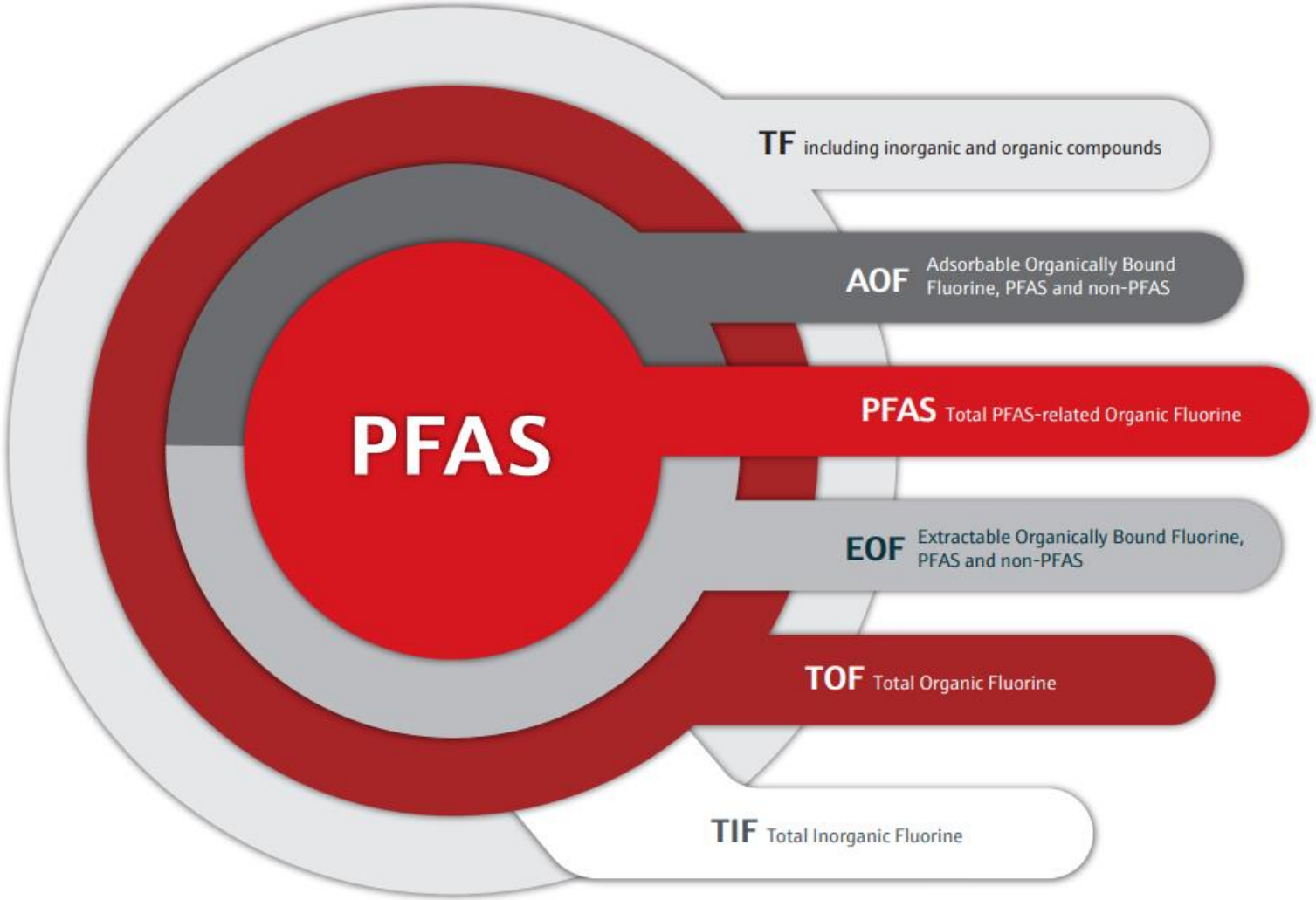
- Related to DIN 38407-42(F42) for water
- Related to DIN 38414-14(S14) for soil and sludge

HPLC – MS / MS



Quantitation of PFASs in Water Samples using LC-MS/MS ; Simon Roberts1 , KC Hyland1 , Craig Butt1 , Scott Krepich2 , Eric Redman3 , and Christopher Borton1 1SCIEX, USA; 2Phenomenex, USA; 3TestAmerica Laboratories, Sacramento, USA

Sum parameter for organic fluorine compounds



- Depending on the regulation and/ or samples coulometric titration or ion chromatography is needed
- AOF and AOX are usually used in:
  - Water treatment facilities,
  - Water monitoring institutions
  - Contract labs
- EOF is usually used in:
  - Academics, research
  - Laboratories, not restricted to standardized routines

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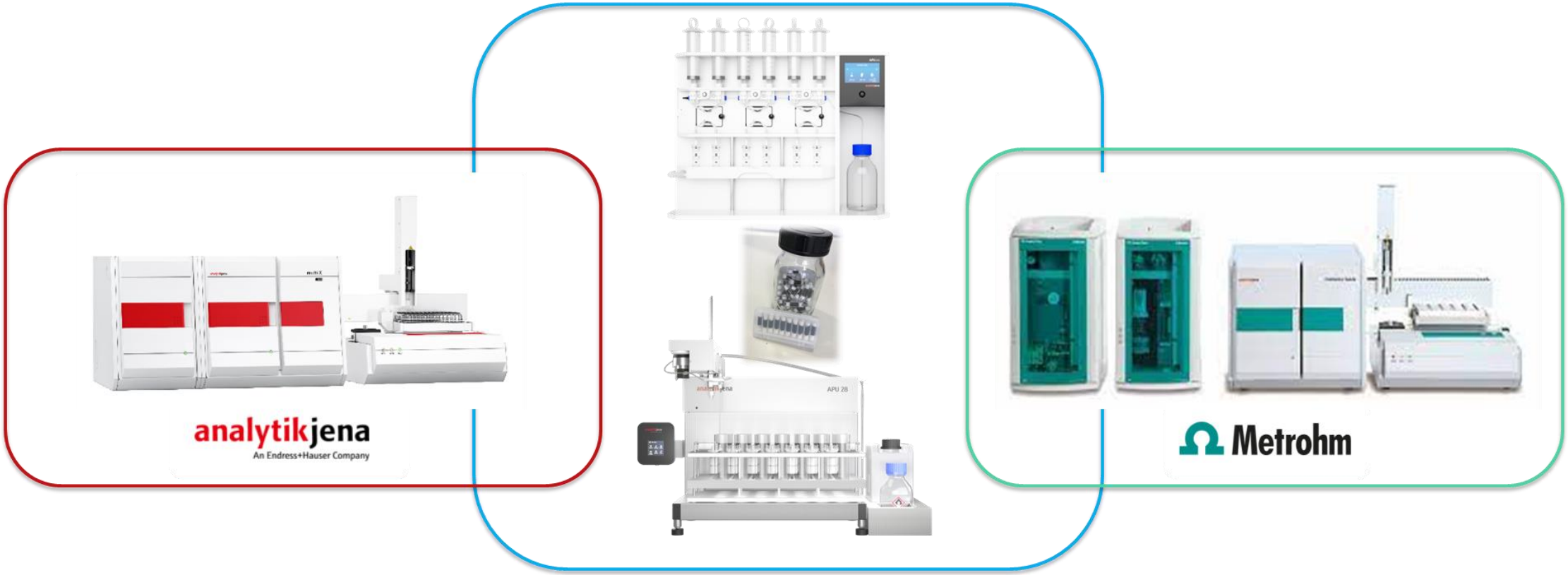
Further application beyond AOX – AOF, AOCl, AOBr and AOI

- Sample preparation units - APUsim and APU28connect are perfectly suited to prepare AOF (AOBr, AOI, AOCl) samples



CIC-Systems and AJ sample prep solutions

- Combination with all CIC systems possible
- Due to its geometry (18x6mm) and material (quartz glass) AJ´s active carbon containers can be placed directly in sample boats/ cups without manual treatment!!!!!

402-880.616 Set 100 pcs;
disposable tubes for AOF, filled

Sample preparation for AOX / AOF – APUsim and APU28connect

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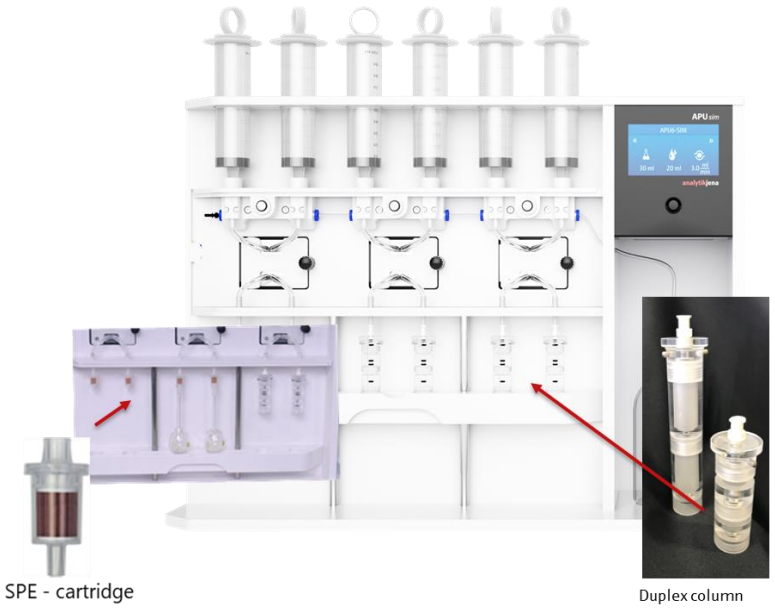

EOF Method using SPE and MAS

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SPE with APU sim and MAS with contrAA 800

Analysis of Per- and Polyfluorinated Compounds (PFC)

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Development of a SPE HR-CS-GFMAS method for EOF determination

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surface water sample (0.45 µm)

separation of fluoride & organically bound fluorine

enrichment & elution of organically bound fluorine

direct analysis via HR-CS-GFMAS

SPE

Developed by Dr. Björn Meermann and team

Sample Preparation with Solid Phase Extraction

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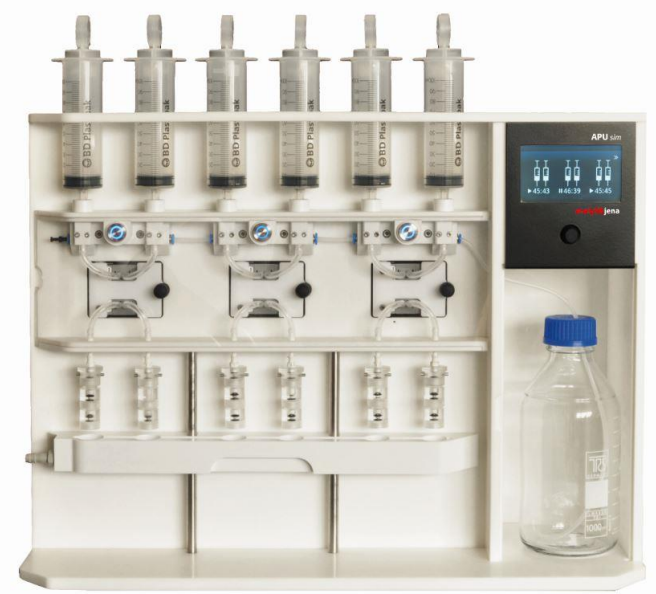
APUsim for EOF - Effortless sample preparation for AOX and SPE methods

- Adsorption / Extraction of **up to 6 samples simultaneously**
- **3 channels** operated individually; 2 lines operated in parallel
- Each channel can handle different settings for
  - Conditioning
  - Adsorption
  - Extraction
  - Rinsing of columns
- Adjustable volumes and flow rates
- Intuitive operation and maximum flexibility
- Minimum maintenance effort



APUsim

Sample Preparation with Solid Phase Extraction

APUsim for EOF - Method settings for EOF sample preparation of river water samples

Cartridge conditioning	Adsorption	Rinsing	Extraction
▪ 10 ml methanol ▪ 100 ml acidified pure water	▪ 500 – 2500 ml sample volume	▪ 100 ml acidified pure water	▪ 5 ml methanol ▪ 5 ml acidified pure water

EOF measurement by MAS with contrAA 800

Chromabond C18 cartridge

MAS- Molecular Absorption Spectroscopy

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Fluorine analysis with High resolution – continuum source AAS (HR-CS-AAS) of contrAA series

MAS- Molecular Absorption Spectroscopy

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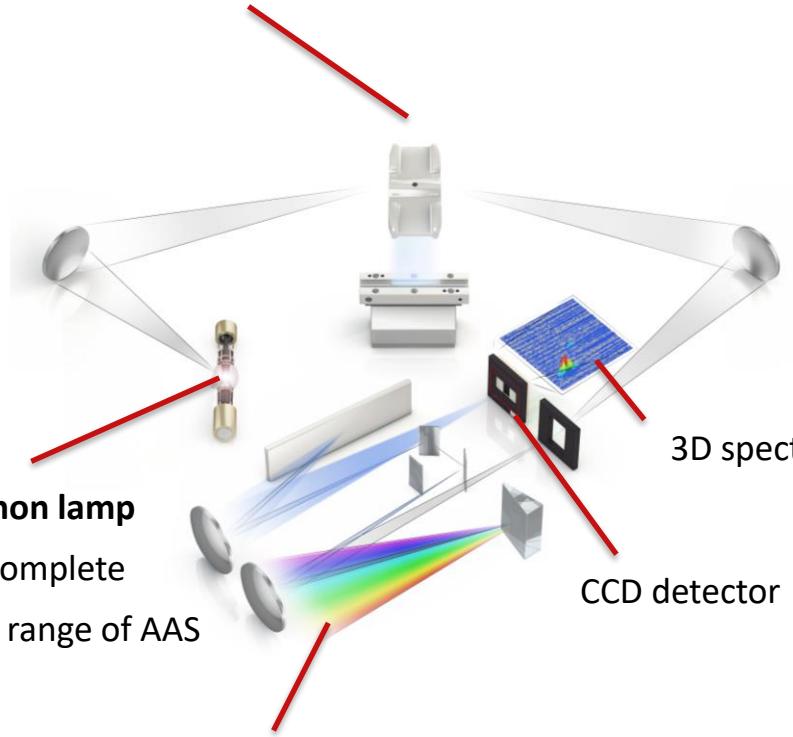
Fluorine analysis with High - Resolution Continuum Source AAS (HR-CS-AAS) of contrAA series

Benefits

- No element-specific components
- Any wavelength available – including molecules
- Fast sequential / simultaneous multi-element analysis
- Spectral background correction

Flame or Graphite Furnace atomizer in Dual configuration available



3D spectrum display

One Xenon lamp covers complete spectral range of AAS

CCD detector

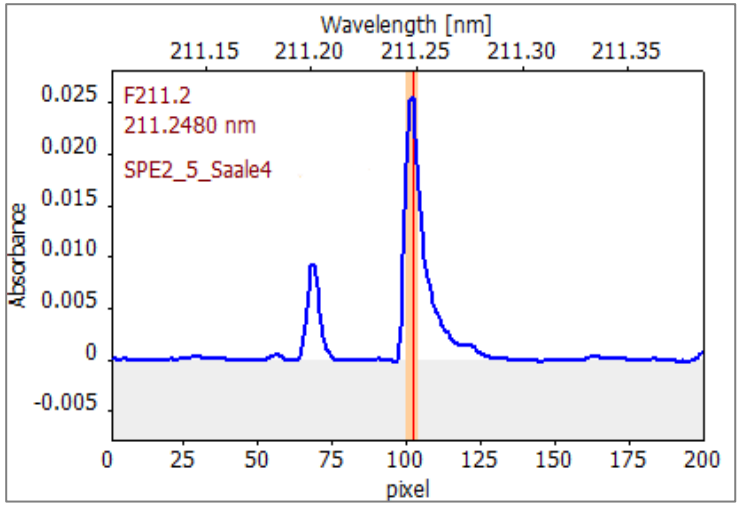
High-Resolution Echelle spectrometer

Based on patented ISAS Technology
ISAS
Institute for Analytical Sciences

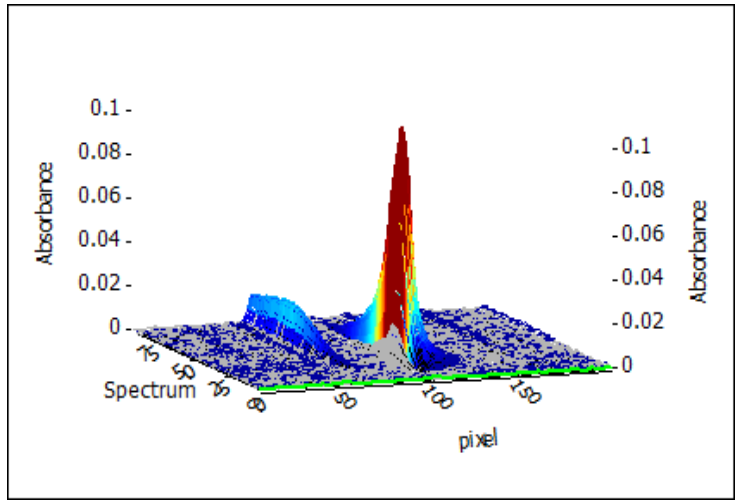
MAS- Molecular Absorption Spectroscopy

Molecular Absorption Spectroscopy for non-metals that cannot be detected by traditional AAS

- Quantitative determination of Fluorine with in-situ conversion into the molecule GaF or CaF
- Detection of molecule absorption line at 211.248 nm (GaF) or 606.440 nm (CaF) with contrAA 800



2D spectrum GaF



3D spectrum GaF

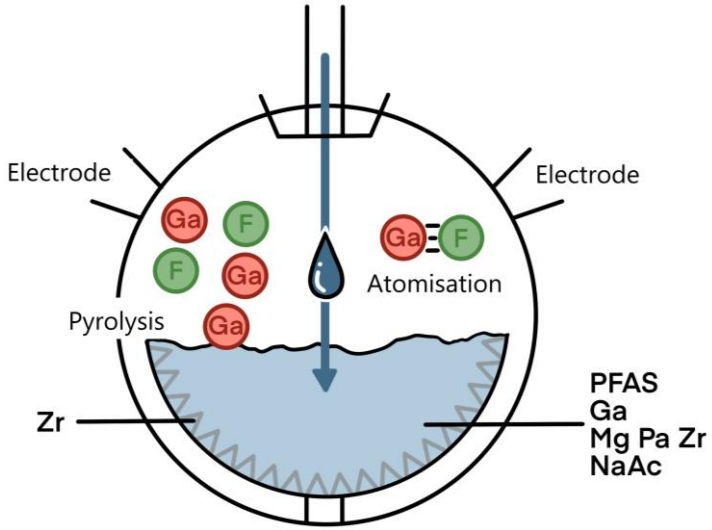
MAS- Molecular Absorption Spectroscopy

Automatic addition of all reagents with autosampler AS-GF:

- Graphite tubes were coated with zirconium (35 µL stock solution, six times)
- Conditioning of the tube using calcium solution (25 µL of 20 mg/L Ca solution) and Pd/ Mg/Zr modifier (15 µL)
- Automated adding of modifier (Pd/Mg/Zr) and reagent Gallium - stock solution

Autosampler AS-GF

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



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

MAS- Molecular Absorption Spectroscopy

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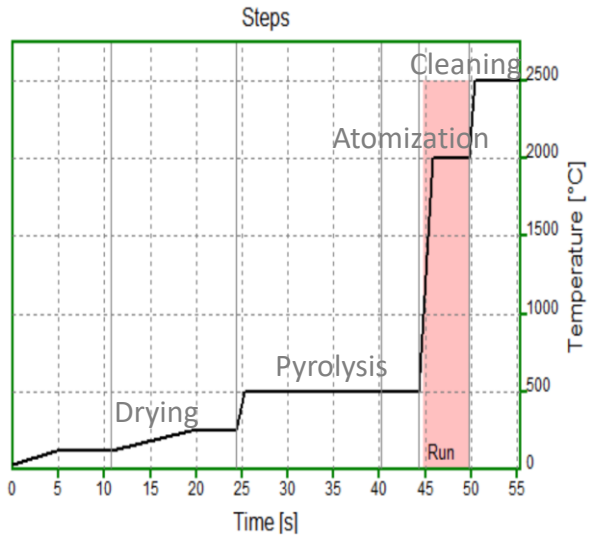
- Fully automated analysis steps and furnace program for the detection of GaF



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.

Furnace program

MAS- Molecular Absorption Spectroscopy

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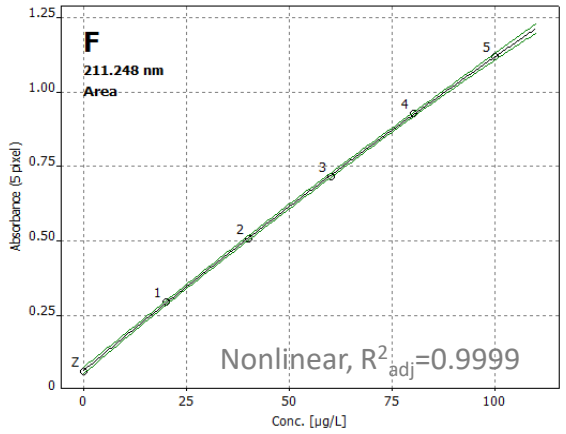
Calibration

- Pre-mixed an organic F from Standard stock solutions (100 µg/L and 200 µg/L) in 0.5% HNO3
- Calibration curve F

  (as GaF molecule)

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



Calibration: 0-100 µg/L F
Detection limit: 0.3 µg/L

EOF in Surface Water

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EOF in Surface Water

Sample sampling date	Enrichment factor	Measured value [µg/L] F^-	RSD [%]	EOF [ng/L]
Saale June,30,2020	250	42.59	2.9	170.4
Saale July,13,2020	250	43.62	4.7	174.5
Saale July,15,2020	150	24.04	3.6	160.2
White Elster Juli12,2020	250	60.76	2.6	243.0
Saarbach Juli12,2020	250	28.66	5.7	114.6

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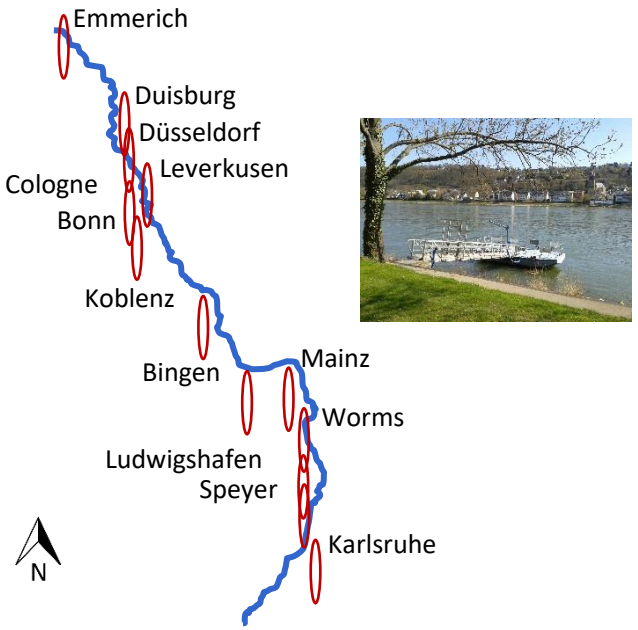
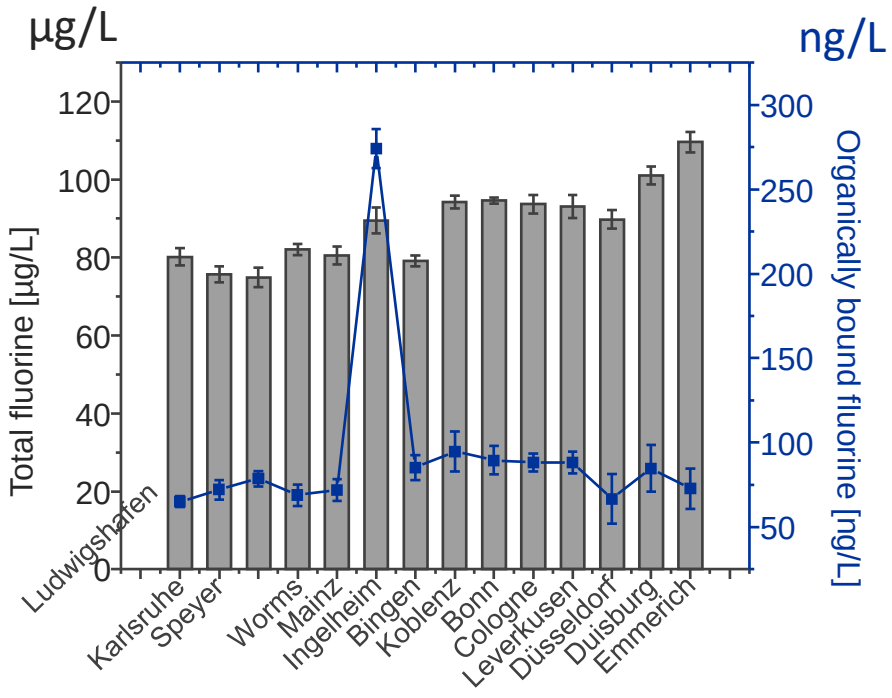
Organically bound fluorine (EOF) along the river Rhine

SPE enrichment factor EOF: x 500

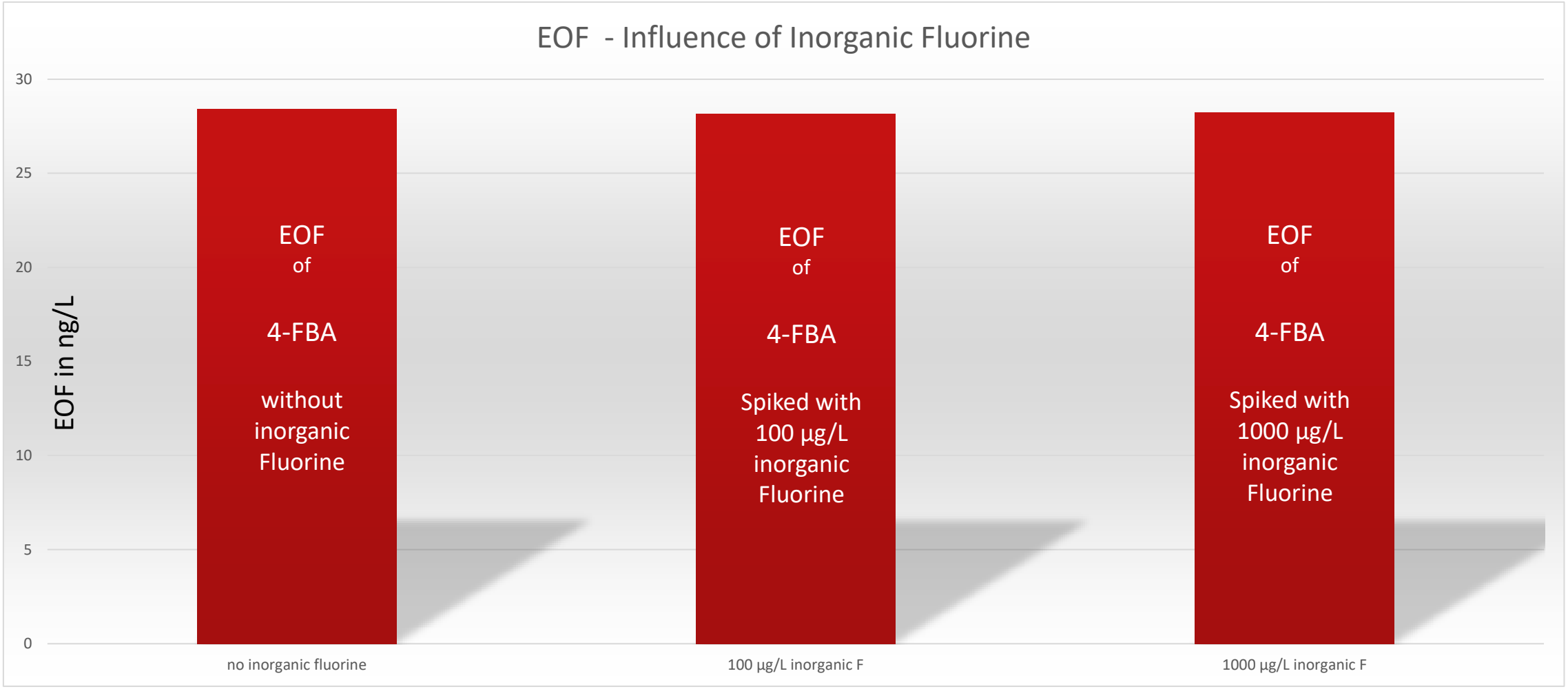




BAM
Bundesanstalt für Materialforschung und -prüfung

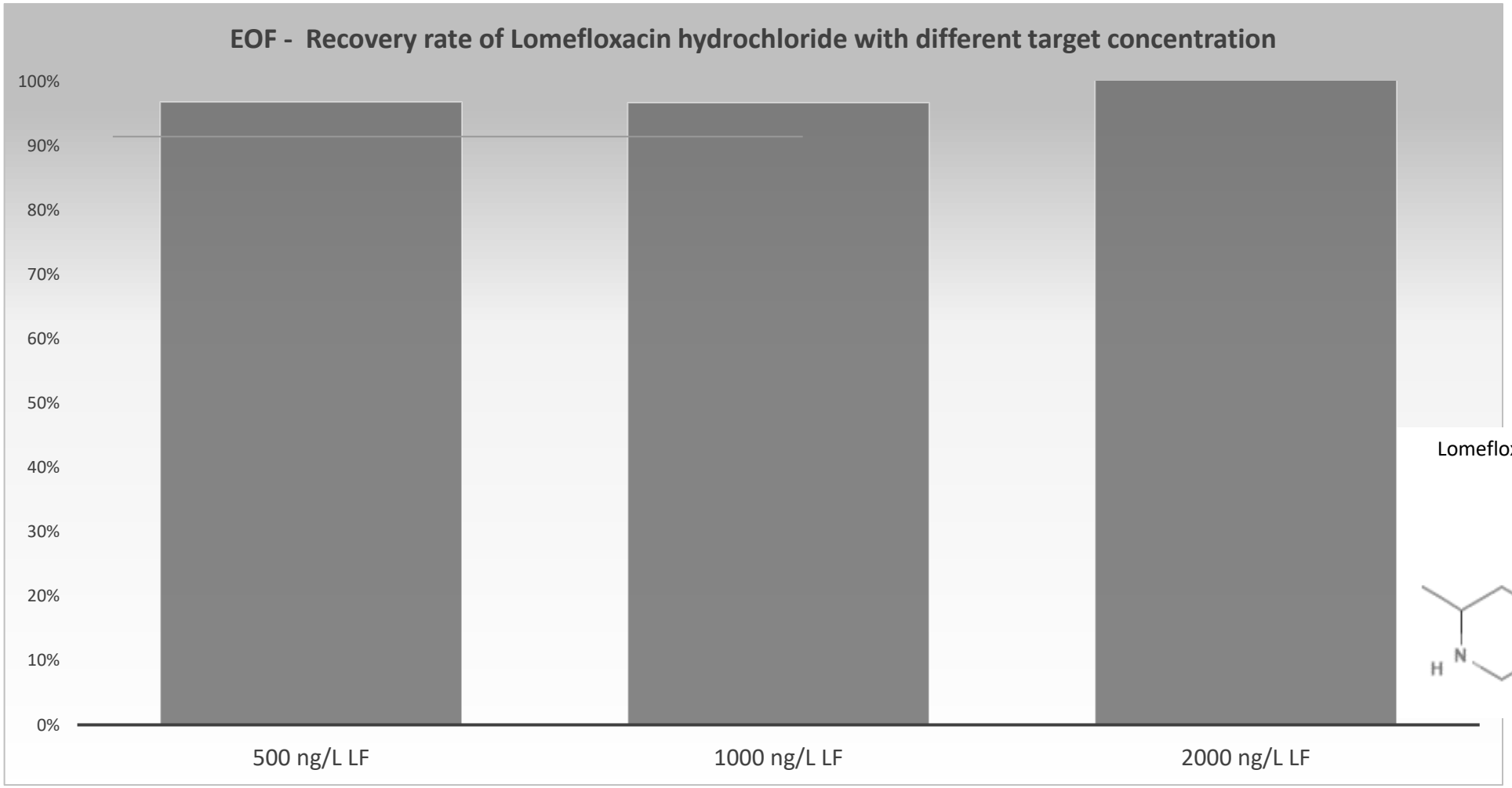
Metzger M., Ley P., Sturm M., Meermann B. *Anal. Bioanal. Chem.* **2019**, 411, 4647-4660.

EOF – Influence of Inorganic Fluorine

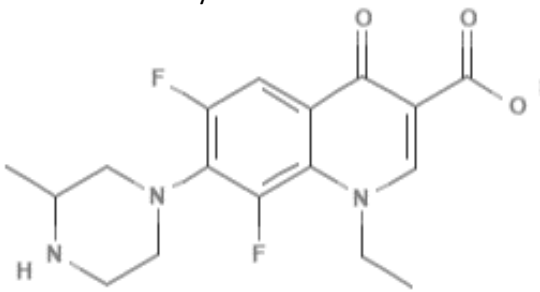


4-FBA = 4 - fluoro benzoic acid

EOF – Fluorinated Organic Standards



Lomefloxacin hydrochloride



EOF – Correlation of Different Detection Methods

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Total fluorine in rivers Rhine and Moselle HR-CS-GFMAS vs. IC

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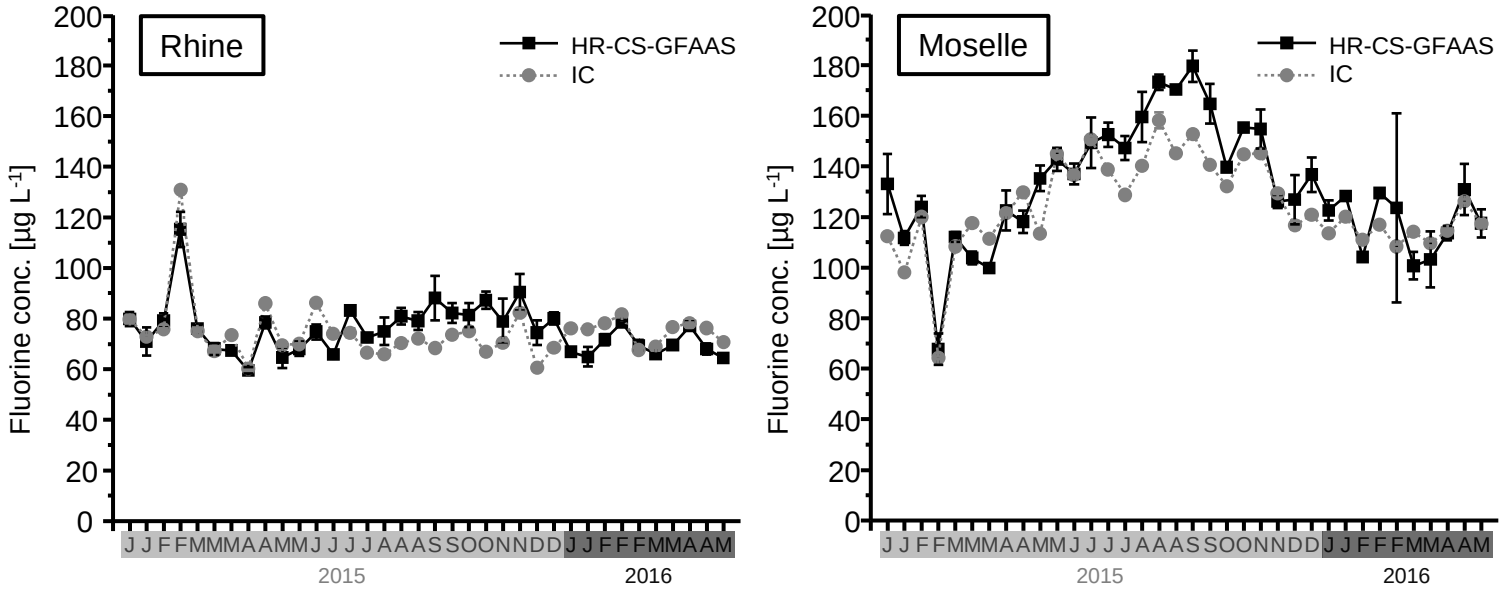

Ley P., Sturm M., Ternes T.A., Meermann B. *Anal. Bioanal. Chem.* **2017**, 409, 6949-6958.

EOF in Sewage Sludge and Soil

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EOF in Sewage Sludge and Soil

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Enrichment by Extraction

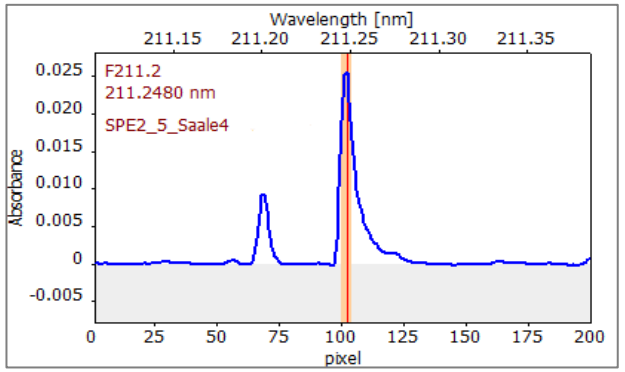
Detection

MAS (Molecular Absorption Spectroscopy)

Using Graphite Furnace-AAS contrAA 800

- Extraction solution: acetic acid-methanol mixture
- Drying of the extract
- Resuspension in methanol-water mixture

contrAA 800 with Xenon lamp as continuum light source



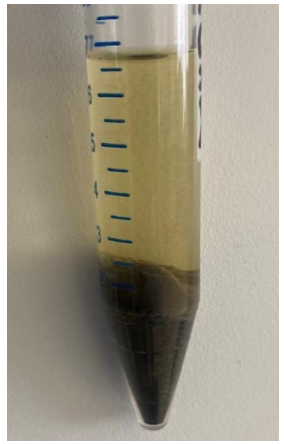
Quantitative Determination of Fluorine as GaF

EOF in Sewage Sludge and Soil

- Extraction as 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

Sewage Sludge 1



Sewage Sludge 2

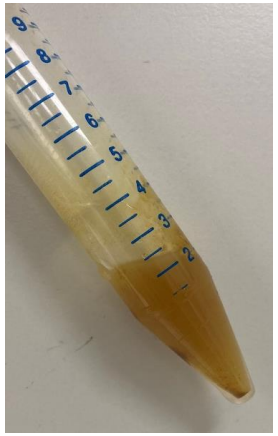
Soil

EOF in Sewage Sludge and Soil

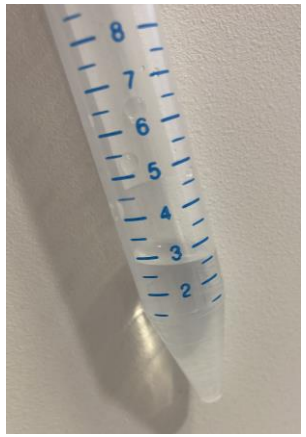
- Extraction as sample preparation

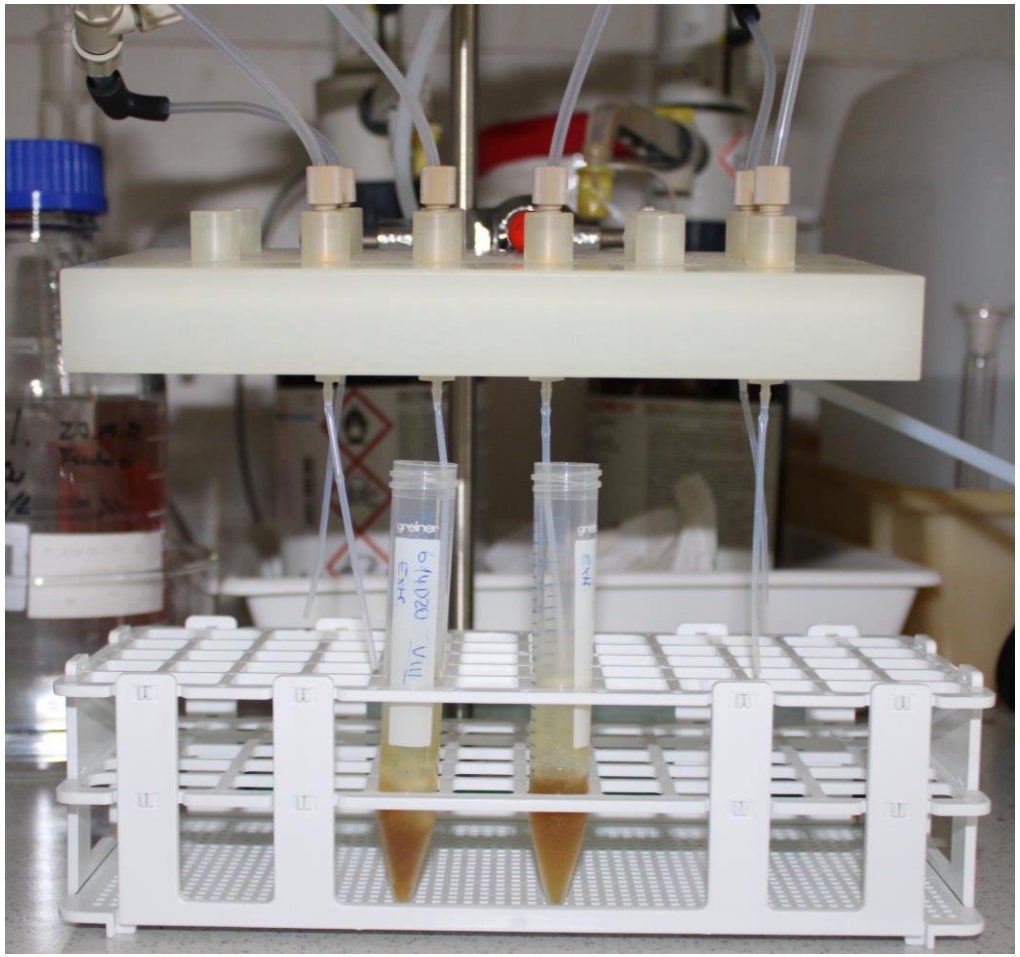
Extract drying	Complete evaporation under Ar stream
Resuspension solution	2 mL of methanol-water mixture 1:1 (v:v)

Sewage Sludge 1



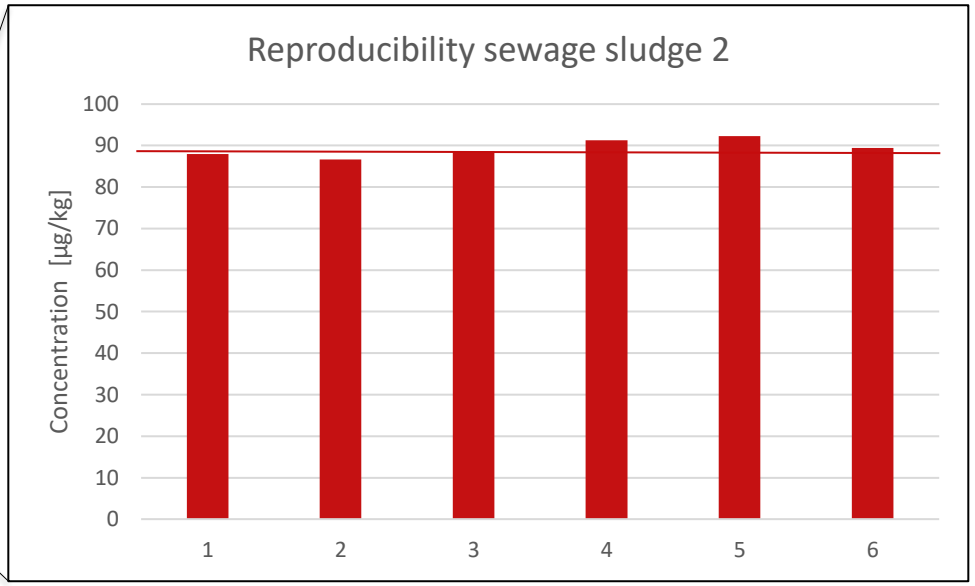
Soil





EOF in Sewage Sludge and Soil

Sample	Sample weighing [mg]	Meas. value [µg/l]	Sample concentration [µg/kg]
Sewage sludge 1	1337.8	68.23	102.0
Sewage sludge 2	1010.3	43.77	86.65
Soil sample	1005.3	6.282	18.75



RSD = (2.14 %)

Thank You Very Much for Your Attention

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