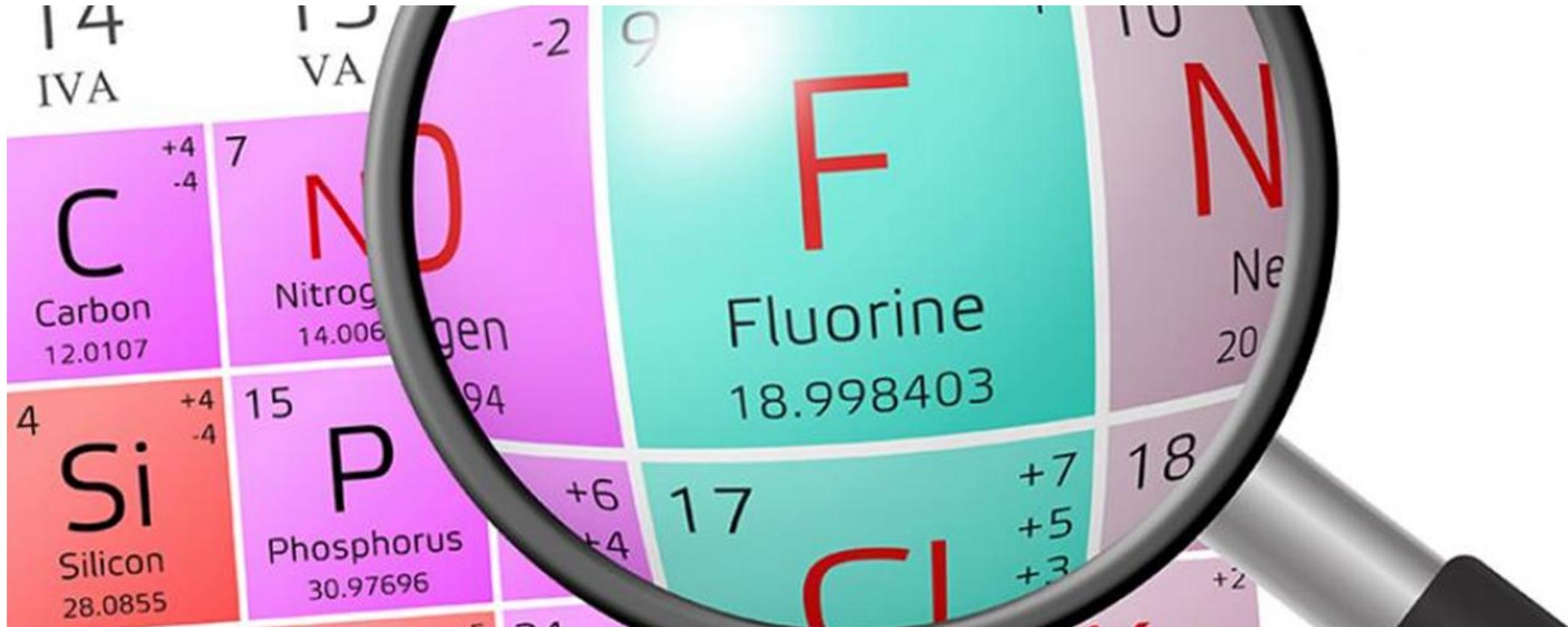


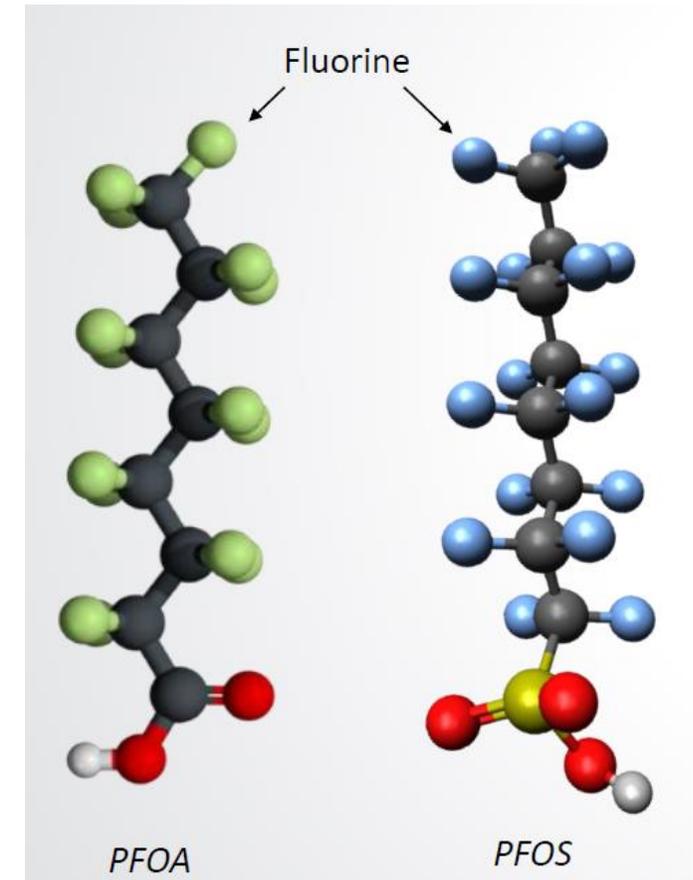
Determination of Extractable Organically Bound Fluorine (EOF) in Surface Water With Molecular Absorption Spectrometry

Speaker: Oliver Buettel, Analytik Jena US



PFAS are a very large class of synthetic chemicals

- **Chains** of carbon (C) atoms surrounded by fluorine (F) atoms, with different terminal ends
- **Complicated chemistry** –thousands of different variations exist in commerce
- **Widely used** in industrial processes and in consumer products
- **Mobile** via multiple air, water pathways
- **Some PFAS** are known to be **PBT**:
 - **Persistent** in the environment
 - **Bio-accumulative** in organisms
 - **Toxic** at relatively low (ppt) levels



PFAS are a very large class of synthetic chemicals

- **Chains** of carbon (C) atoms surrounded by fluorine (F) atoms, with different terminal ends
- **Complicated chemistry** –thousands of different variations exist in commerce
- **Widely used** in industrial processes and in consumer products
- **Mobile** via multiple air, water pathways
- **Some** PFAS are known to be **PBT**:
 - **Persistent** in the environment
 - **Bio-accumulative** in organisms
 - **Toxic** at relatively low (ppt) levels

Drinking Water Health Advisories and \$1B in Funding

On June 15, 2022, EPA released four drinking water health advisories for PFAS. EPA also announced that it is inviting states and territories to apply for \$1 billion in Bipartisan Infrastructure Law grant funding to address PFAS and other emerging contaminants in drinking water.

Current EPA methods

■ Drinking (Potable) Water Methods

- Method 533: Determination of PFAS in Drinking Water by Isotope Dilution Anion Exchange SPE and LC/MS/MS (2019)
- Method 537.2: Determination of Selected PFAS in Drinking Water by SPE and LC/MS/MS (2020)

■ Total Fluorine Methods

- Total Organic Fluorine (TOF) (EPA started to develop this method in 2021)
- Total Organic Precursors (TOP) (TOP methods are commercially available. EPA considered the need for a thorough multi-laboratory validation study in 2021)
- Draft Method 1621 Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)

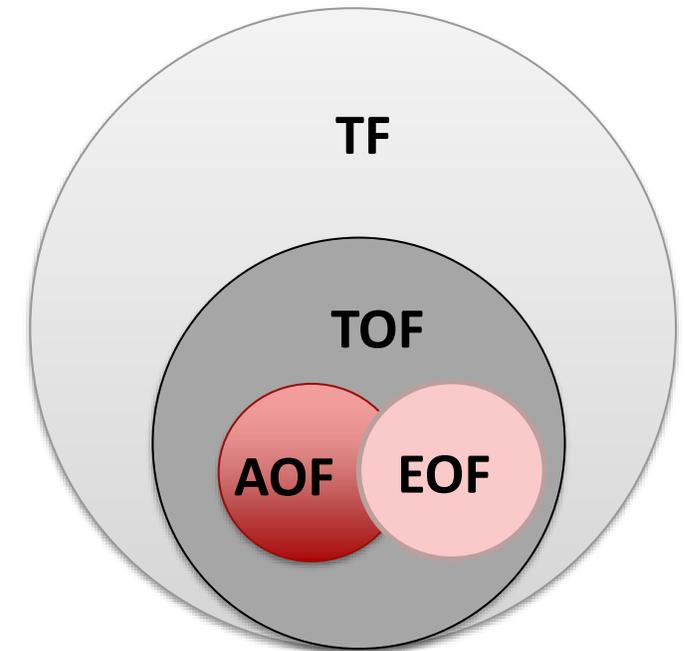
Reference: EPA

■ Extraction Techniques:

- AOF: Adsorption of organically bound fluorine on activated carbon
- EOF: Extraction of TOF using SPE/solvents

■ Detection Techniques:

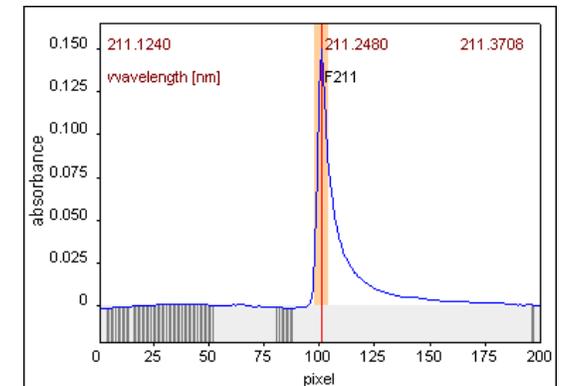
- Combustion Ion Chromatography (CIC)
- High-Resolution Continuum Source Molecular Absorption Spectrometry



Reference: Finding the most suitable PFASs sum parameter method – A comparison of AOF vs. EOF and CIC vs. HR-CS-GFMS

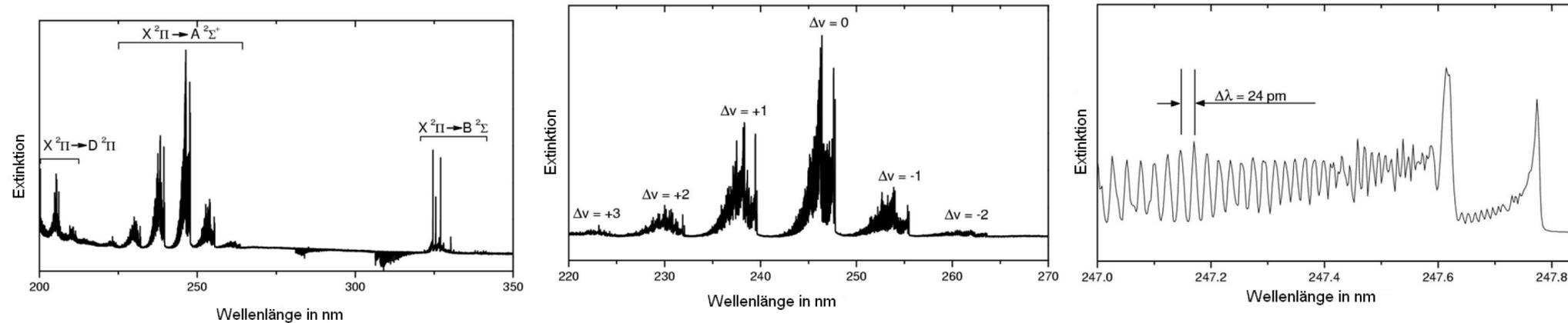
High-Resolution Continuum Source Molecular Absorption Spectrometry

- Atomic absorption techniques are based on the absorption of atomic spectral lines by gas-phase atoms in their ground electronic states. The atomic vapor is usually generated thermally in a flame (flame AAS) or graphite furnace tube (furnace AAS).
- **Direct** determination of nonmetals, such as **fluorine**, is impossible because their resonance lines are located in the vacuum-UV range
- Conversion of Fluorine into characteristic, diatomic molecules
 - ✓ GaF, CaF, AlF, SrF ...
 - ✓ Species-independent → Total Fluorine



Spectra of Diatomic Molecules

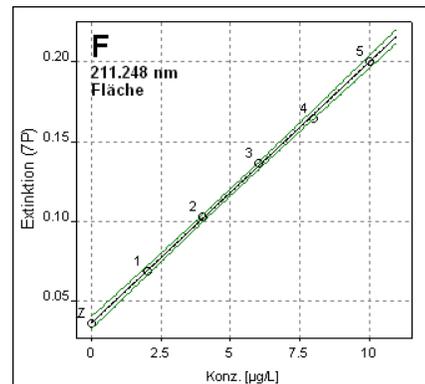
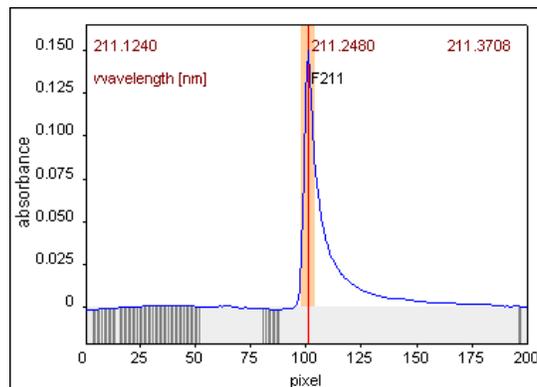
- Coupling of Electronic transitions, Vibrational and Rotational fine structures (example: PO)
- Full width at half maximum similar to atomic absorption/emission lines → Selectivity, Specificity → **high resolution**



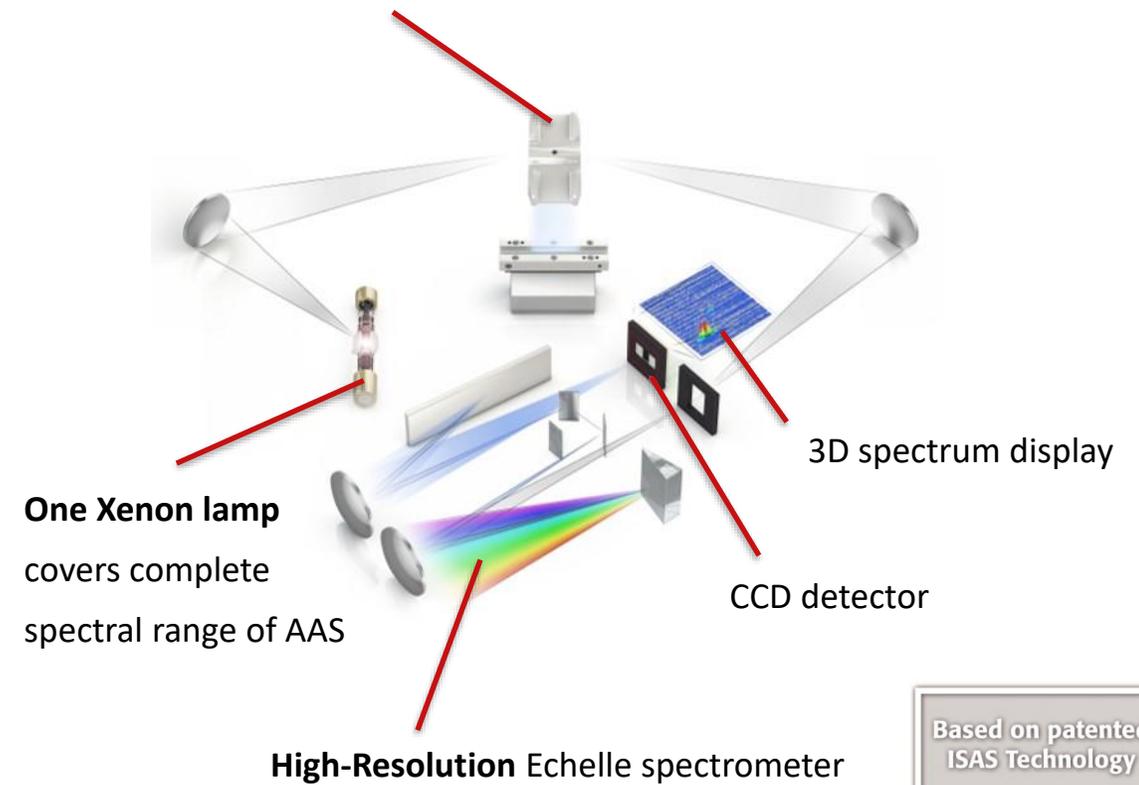
High-Resolution Continuum Source AAS (HR-CS-AAS)

- HR-CS AAS: Analytik Jena contrAA 800 G
 - Xenon light source : Any wavelength available for analysis (185-900 nm)
 - CCD detection: spectral resolution 2 pm at 200 nm
 - Wide working range: 0.3 µg/L– 100 mg/L(GaF)

GaF 211.248 nm



Flame or Graphite Furnace atomizer in Dual configuration available



Based on patented
ISAS Technology
ISAS
Institute for Analytical Sciences

Extraction

Parameter	Specification
Device	APU sim
SPE cartridges	Chromafix HR-P (polystyrene-divinylbenzene absorbent resin, Macherey-Nagel)
Flow speed	3mL/ min (conditioning, elution), 5 mL/ min (sa
Sample volume	500 – 2500 mL
Conditioning volume	10 mL methanol
Elution volume	5 mL methanol, 5 mL acidified water



Analytik Jena APU sim

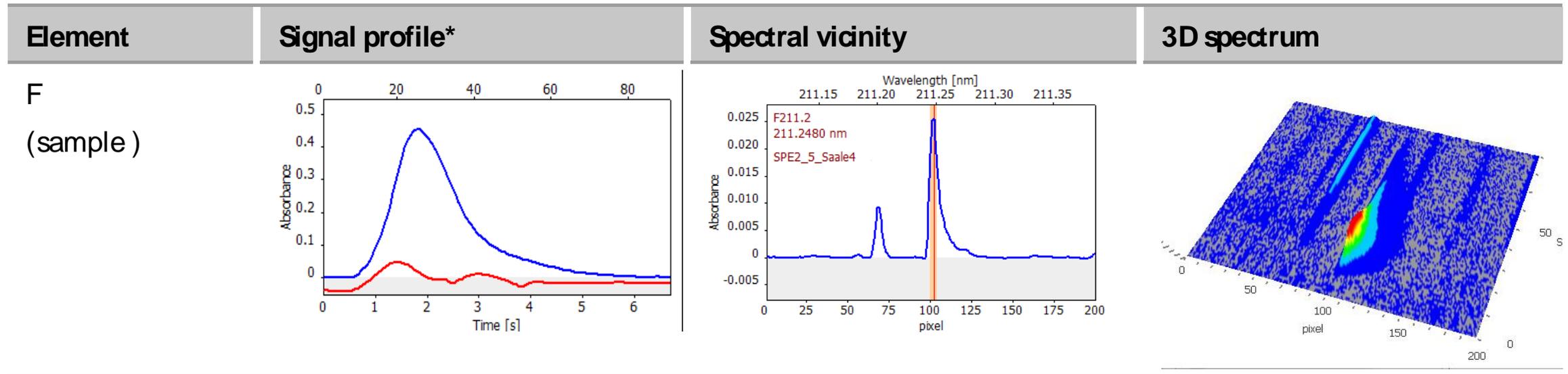
Method Settings

Molecule	Wave-length [nm]	No. of eval. pixels	T _{Pyr.} [°C]	T _{Atomis.} [°C]	Ramp [°C/s]	Meas. time [s]	Modifier	Baseline correction
GaF	211.248	5	500	1600	1500	6.5	3 µL Pd/ Mg/ Zr modifier 9 µl Ga solution 3 µl NaAc solution	IBC

Step	Name	Temp (°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	1600	1500	6	stop
7	Clean	2450	500	5	max

Spectra of Inorganic and Organic Mixture Calibration Standard

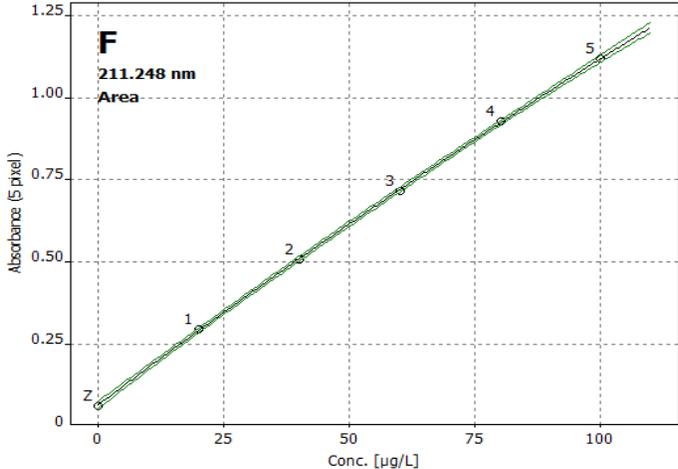
- Low background absorbance (red)
- Clear, interference-free GaF absorbance signal (blue)



* blue: analyte signal, red: background signal

Calibration curve

LOD: 3.247 µg/L

Element	Type of calibration	Correlation R^2_{adj}	Graphical display
F (as GaF molecule)	nonlinear	0.999858	

Recovery rates for organic standards

Sample	Enrichment factor	Measured value [$\mu\text{g/L}$]	RSD [%]	Sample actual concentration [ng/L]	Sample target concentration [ng/L]	Recovery rate [%]
4-FBA_1	50	31.36	5.6*	627.2	1000	62.7
4-FBA_2		29.92	2.2*	598.4		59.8
4-FBA_3		32.13	2.2*	642.6		64.3
4-FBA_{avg}		31.79	6.2**	635.8		63.6
PFBS_1	50	20.16	4.4*	403.2	1000	40.3
PFBS_2		19.79	2.2*	395.8		39.6
PFBS_3		21.58	6.3*	435.6		43.6
PFBS_{avg}		20.58	5.1**	411.6		41.2
LF0.5_1	50	23.43	4.2*	468.6	500	93.7
LF0.5_2		24.96	2.6*	499.2		99.8
LF0.5_{avg}		24.19	3.8**	483.9		96.8
LF1_1	50	45.56	4.5*	911.2	1000	91.1
LF1_2		51.14	1.2*	1,023		102.3
LF1_{avg}		48.35	5.9**	967.0		96.7
LF2_1	50	110.8	1.3*	2,216	2000	110.8
LF2_2		111.1	1.9*	2,222		111.1
LF2_{avg}		110.9	1.2**	2,219		110.9

Influence of inorganic fluorine

Sample	Enrichment factor	no inorganic fluorine		10 ² exceed of inorganic F		10 ³ exceed of inorganic F	
		Measured value [µg/ L]	RSD _(n=3) [%]	Measured value [µg/ L]	RSD _(n=3) [%]	Measured value [µg/ L]	RSD _(n=3) [%]
4-FBA_1	50	28.40	1.0	29.33	0.6	27.56	2.4
4-FBA_2		25.31	2.0	28.71	6.2	28.83	0.8
4-FBA_3		31.17	1.4	26.44	1.5	28.25	1.8
4-FBA_{avg}		28.29	7.6	28.16	4.8	28.21	2.2

Measurement of surface water samples

Sample <small>sampling date</small>	Enrichment factor	Measured value [$\mu\text{g}/\text{L}$]	RSD [%]	Sample concentration [ng/L]
Saale <small>June,30,2020</small>	250	42.59	2.9	170.4
Saale <small>July,13,2020</small>	250	43.62	4.7	174.5
Saale <small>July,15,2020</small>	150	24.04	3.6	160.2
White Elster <small>Juli12,2020</small>	250	60.76	2.6	243.0
Saarbach <small>Juli12,2020</small>	250	28.66	5.7	114.6

Matrix effects

The recovery rate of organically bound fluorine in nature matrix was **86%**.

Sample	Enrichment factor	Measured value [$\mu\text{g/ L}$]	RSD [%]	Sample actual concentration [ng/ L]	Spike [ng/ L]	Sample target concentration [ng/ L]
Saale _{control}	150	23.09	4.37	153.9	0	-
Saale_LF	150	62.89	3.88	419.3	333.3	487.3

1. Optimized furnace program to provide high sample throughput and accuracy
 - Sample analysis time: **3 minutes/measurement**
 - Spike **recovery rate 86 %** by spiking of river water sample with a known concentration of test fluorinated organic substance (lomefloxacin 333 µg/L F).
2. Highly sensitive method: low LOD, **3.2 ppb**
3. Easy operation:
 - No cleaning steps required
 - Dilution and spike can be easily achieved with the autosampler



Thank you for your attention!

Extraction

Parameter	Specification
device	APUsim
SPE cartridges	Chromafix HR-P (polystyrene-divinylbenzene absorbent resin, Macherey-Nagel)
Flow speed	3mL/ min (conditioning, elution), 5 mL/ min (sal)
Sample volume	500 – 2500 mL
Conditioning volume	10 mL methanol
Elution volume	5 mL methanol, 5 mL acidified water



Table 3

Graphite furnace temperature program of total fluoride determination by means of MAS of AlF at 227.460 nm.

	Temperature [°C]	Ramp [°C/s]	Hold time [s]	Argon flow
Injection of reagent (8 µg Al ³⁺ as Al(NO ₃) ₃)				
Drying	70	1	0	Max.
Drying	110	2	3	Max.
Injection of sample (6 µL) and modifier (8 µg Ba ²⁺ as Ba(NO ₃) ₂)				
Drying	70	1	0	Max.
Drying	110	2	3	Max.
Pyrolysis	600	40	15	Max.
Auto zero	600	0	5	Stopp.
Vaporization	2100	1500	5	Stopp.
Cleaning	2450	100	3	Max.

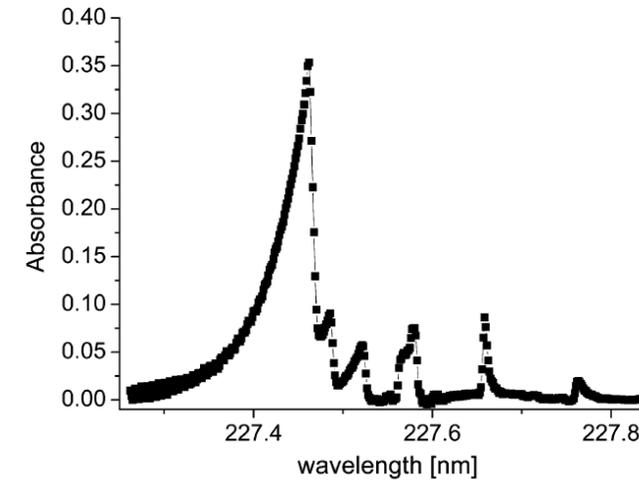


Fig. 4. High-resolution AlF molecular absorption spectrum in a graphite furnace at a pyrolysis temperature of 600°C and a vaporization temperature of 2100°C (assembled from three overlapping spectra; 7.5 ng fluoride, 8 µg aluminum, 8 µg barium).

Step	*	Name	Temp.	Ramp	Hold	Time	Gas		Inj.	E/P
			[°C]	[°C/s]	[s]	[s]	Purge	Add.		
1		Drying	80	6	5	13.3	Max	Stop		
2		Drying	100	6	5	8.3	Max	Stop		
3		Drying	160	10	5	11.0	Max	Stop		
4		Drying	350	25	10	17.6	Max	Stop		
5		Drying	1100	500	12	13.5	Max	Stop		*
6		Drying	70	NP	10	10.0	Max	Stop		
7		Drying	80	2	10	15.0	Max	Stop	*	
8		Drying	110	5	15	21.0	Max	Stop		
9		Pyrolysis	250	50	5	7.8	Max	Stop		
10		Pyrolysis	500	200	5	6.3	Max	Stop		
11		Gas adaption	500	0	5	5.0	Stop	Stop		
12		Atomize	1450	1200	5	5.8	Stop	Stop		
13		Clean	2450	1200	4	4.8	Max	Stop		

ContrAA for F analysis

- This is because with the Xenon lamp you can access any wavelength, including those of molecules. Traditional AAS instruments use hollow cathode lamps that emit line spectra characteristic to the element they contain. So these lamps simply don't produce the wavelengths the molecule is able to absorb.
- Another reason is the low resolution of traditional AA spectrometers, about 100x lower than the contrAA, which is not sufficient to properly isolate the molecule absorption lines.
- Lastly, you need the CCD detector to display the absorption spectrum for accurate background correction. That is also not possible with photomultipliers or similar detectors that are traditionally used in AAS.