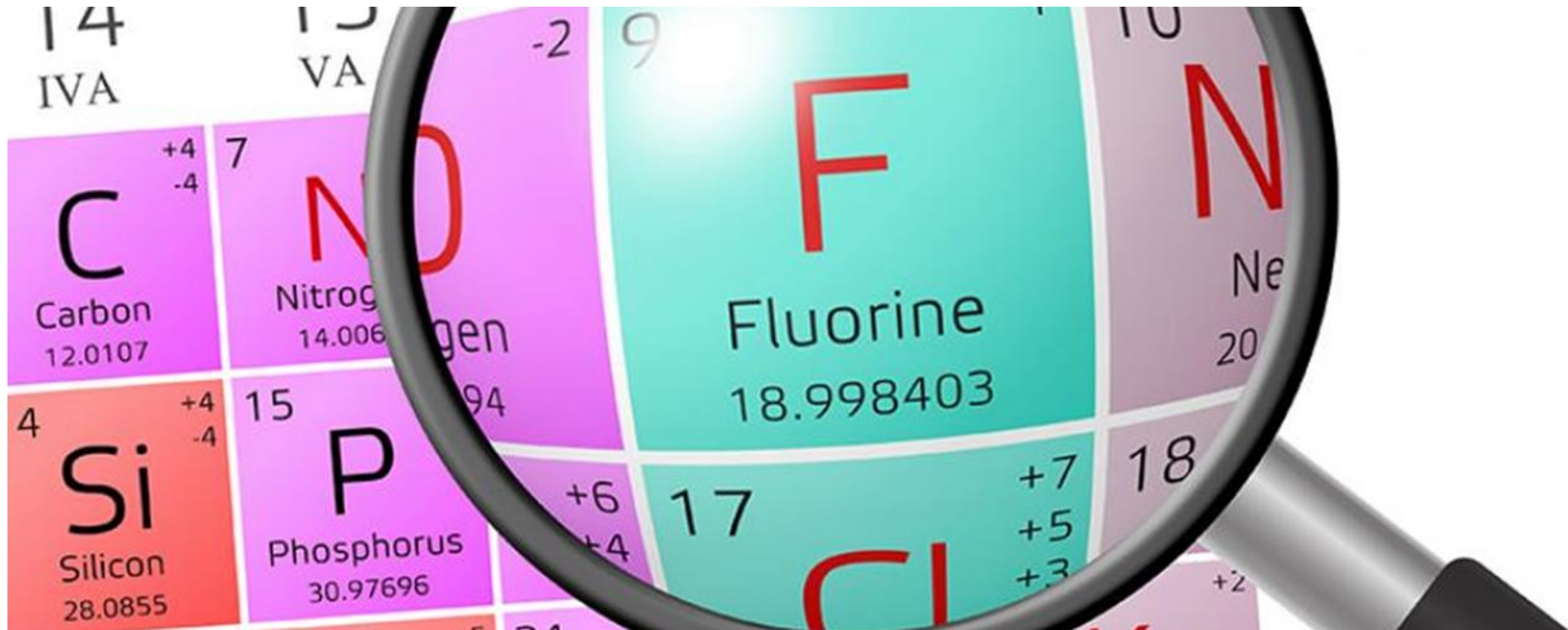


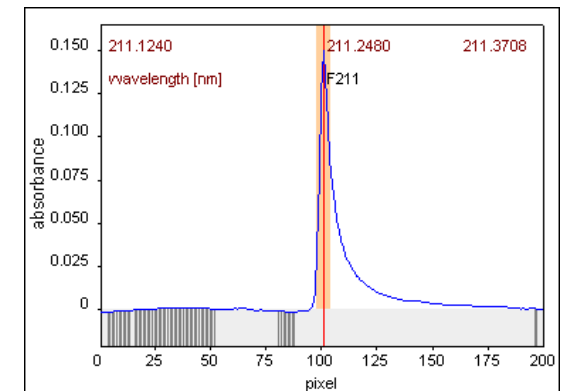
Determination of Total Organic Fluorine in Wastewater by HR-CS MAS

Speaker: Dr. Siqi Sun, Application Scientist at Analytik Jena US



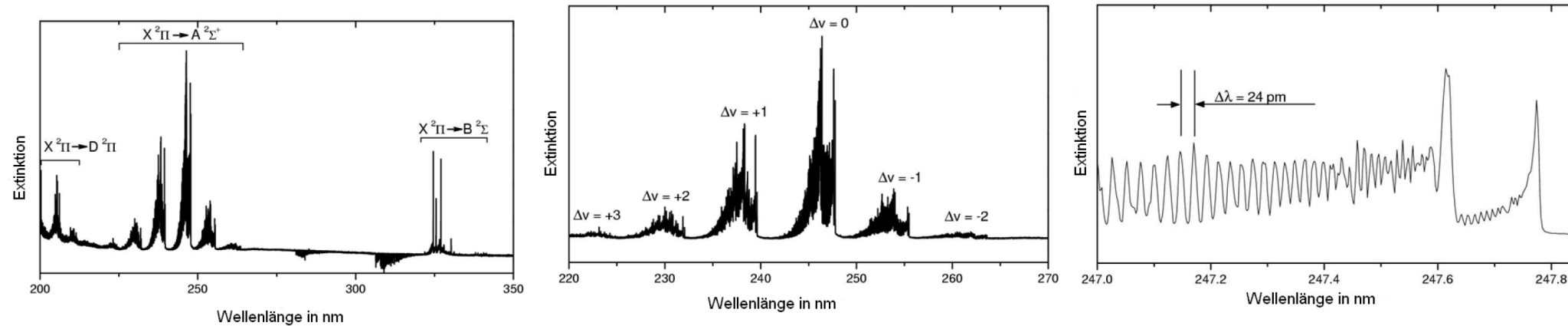
High-Resolution Continuum Source Molecular Absorption Spectrometry

- 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
 - ✓ Speciation through extraction and purification methods (SPE and HPLC)



Spectra of Diatomic Molecules

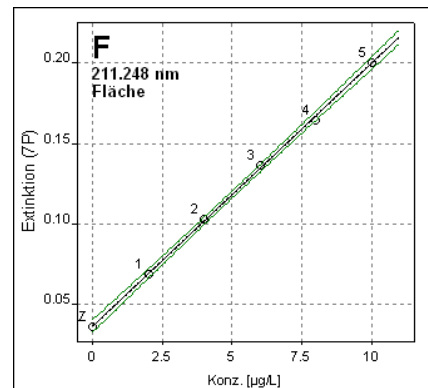
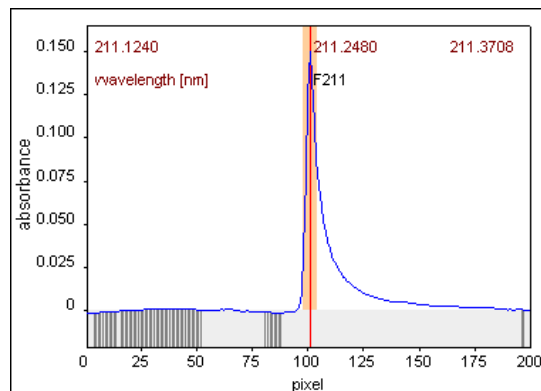
- Coupling of Electronic transitions, Vibrational and Rotational fine structures (example: PO)
- Full width at half maximum similar to atomic absorption/emission lines → Selectivity, Specificity → **high resolution**



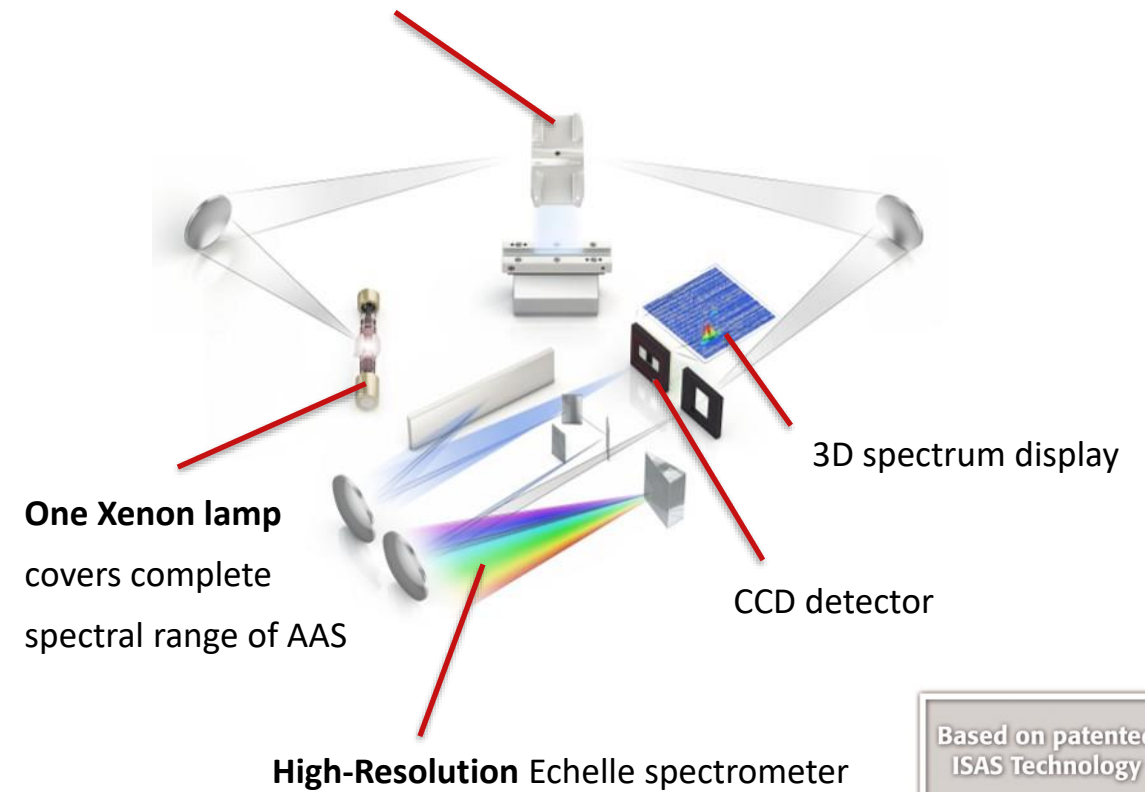
High-Resolution Continuum Source AAS (HR-CS-AAS)

- 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

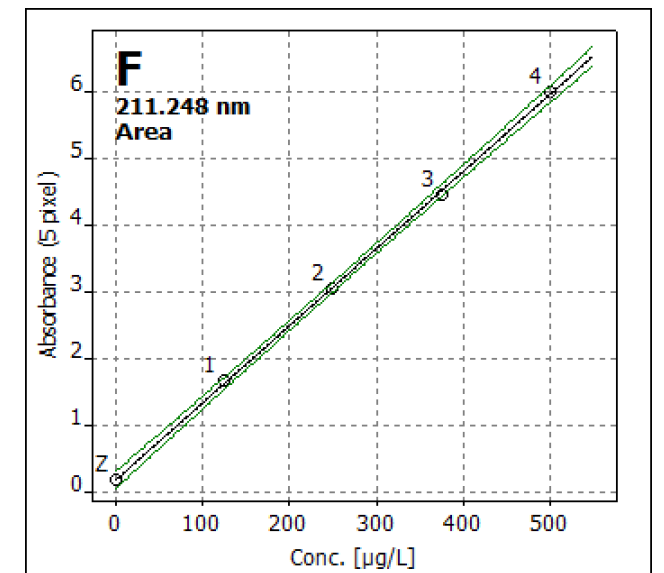


Based on patented
ISAS Technology
ISAS
Institute for Analytical Sciences

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	1450	1200	5	5 µL Pd/Mg/Zr modifier* 5 µl Ga solution* 3 µl Ga solution 5 µl Ba solution	IBC

Step	*	Name	Temp. [°C]	Ramp [°C/s]	Hold [s]	Time [s]	Gas		Inj.	E/P
							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		



Calibration Strategy

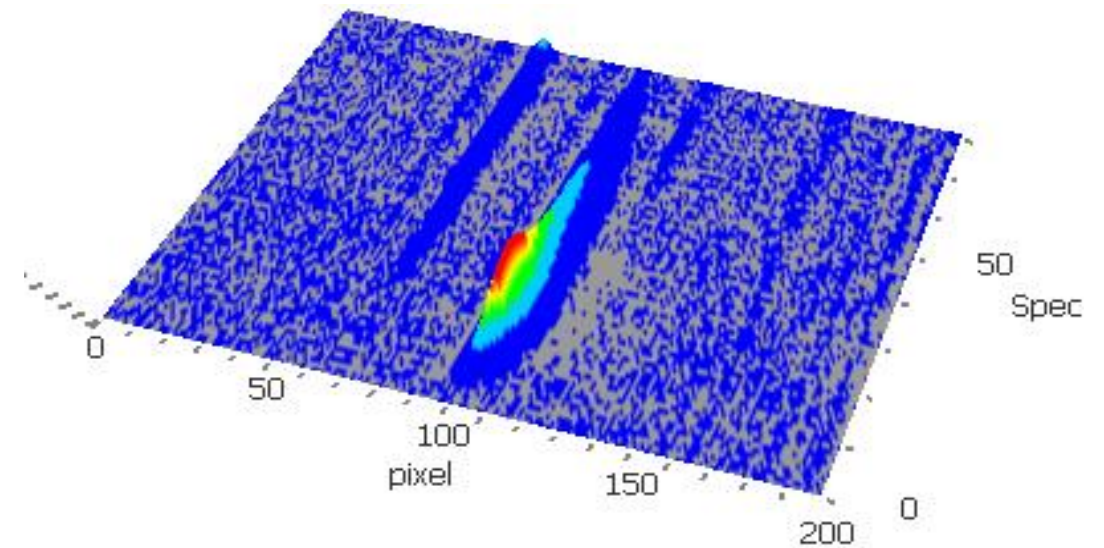
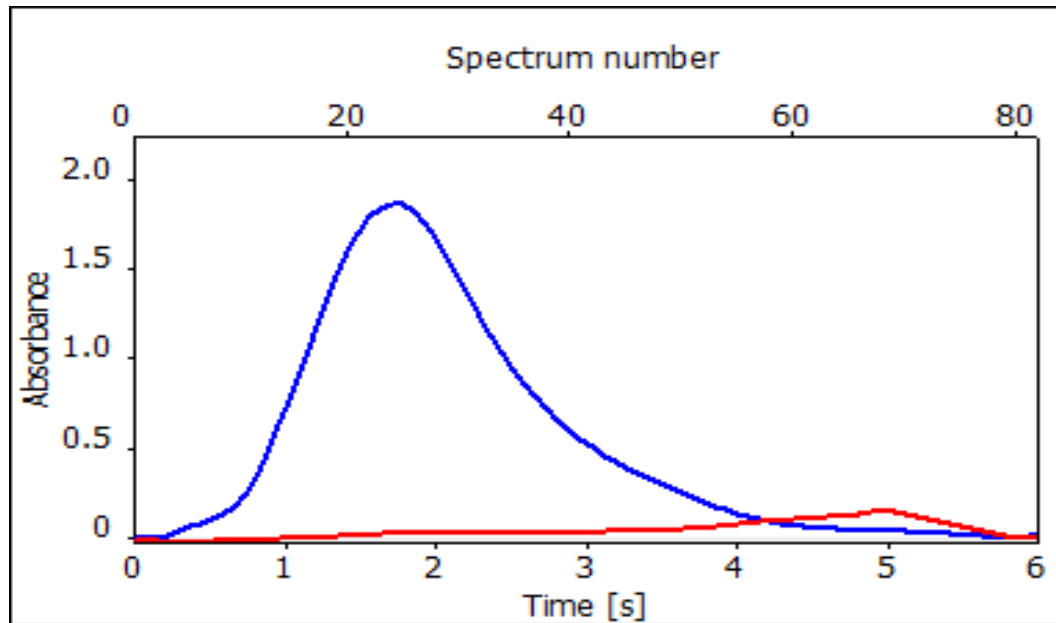
Calibration Set		Component		Ratio
Inorganic F		NaF		
Organic F		PFOS, PFOA, HFPO-DA		1:1:1
Inorganic and organic mixture		NaF, PFOS, PFOA, HFPO-DA		1:1:1:1

Name	Conc.	Inorganic F	Organic F	Inorganic and organic mixture
Unit	µg/L	Abs	Abs	Abs
Cal-Zero1	0	0.1727	0.1154	0.1709
Cal-Std1	125	1.6650	0.5177	1.1601
Cal-Std2	250	3.0402	1.0367	1.7833
Cal-Std3	375	4.4542	1.4847	2.4628
Cal-Std4	500	5.9955	1.9403	3.0694
R ²		0.9993	0.9999	0.9808
LOD (µg/L)		7.737	12.58	4.00

- Different signal response of organic and inorganic F-compounds depends on their thermal stability
 - Volatile PFAS partially lost during drying and pyrolysis steps of furnace program
 - Inorganic F is thermally stable during these steps
- Calibration standards should have composition similar to samples

Spectra of Inorganic and Organic Mixture Calibration Standard

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



Result with Inorganic and Organic Mixture Calibration

Samples	Conc. (µg/L)	Recovery (%)
D.I. water	<LOQ	
QC standard	127.6	99.7
QC standard spike with 125 ppb TF*	252.6	85.0
QC standard spike with 100 ppb NaF	380.9	167.1
Wastewater	1936.5	
Wastewater (1:50) spike with 125 ppb TF*		86.1

- QC standard solution (24 fluorinated organic compounds mixture, TF around 128 ppb)
- Mix of org. and inorg. F for calibration provides best approximation of analyte characteristics
- Good recovery for QC and waste water with TF* spike
- Overestimation of inorg. F due to high thermal stability

*TF = NaF, PFOS, PFOA, HFPO-DA (ratio 1:1:1:1)

Long-term Stability and Repeatability

QC standard	Conc. ($\mu\text{g/L}$)	RSD of 5 replicates
Test 1-Week 1	127.6	3.8 %
Test 2-Week 2	113.8	3.0 %
Test 3-Week 3	120.2	2.7%
Average Conc.	120.5	
RSD of three tests	5.7%	

Three tests all used Test 1's calibration curve without recalibration.

1. Optimized furnace program to provide high sample throughput and accuracy
 - Sample analysis time: **3.5 minutes/measurement**
 - QC average **recovery rate 99.7 %** by inorganic and organic mixture calibration strategy
2. Highly sensitive method: low LOD, **4ppb**
3. Easy operation:
 - No cleaning steps required
 - Dilution and spike can be easily achieved with the autosampler

Future research outlook

- Thermal stabilization of volatile organic fluorinated compounds
- Optimize and simplify sample preparation for Absorbable Organic Fluorine (AOF) and Extractable Organic Fluorine (EOF) analyses of wastewater



Thank you for your attention!