Challenge
Sensitive and reliable determination of total fluorine in drinking water

Solution
High-resolution continuum-source graphite furnace AAS (contrAA 800 G/D) for detection of fluorine via molecular absorption spectrometry (HR-CS MAS)

Intended audience
Laboratories with a requirement for high detection sensitivity for total fluorine analysis

Quantification of Total Fluorine in Drinking Water Using HR-CS MAS

Introduction

The quantification of fluorine in small traces is a challenge for instrumental analysis. Sensitive plasma-based techniques such as ICP-OES or ICP-MS or (total reflection) X-ray fluorescence analysis do not provide a direct or sensitive application for the determination of fluorine.

Techniques such as ion selective electrodes are not robust and sensitive enough to reliably determine this element in the low µg L^{-1} range, and ion chromatography requires appropriate sample preparation for reliable total fluorine determination. Therefore, the alternative and powerful quantification of fluorine via molecular bands such as calcium or gallium fluoride compounds is a promising approach and is presented in this application note. Molecular absorption spectrometry (MAS) with contrAA 800 is a versatile and promising method for instrumental analysis in the 21st century.

The unique design of the contrAA 800 high-resolution continuum source atomic absorption spectrometer (HR-CS AAS) allows absorption bands of molecular vibrations and rotations in the 185-900 nm range to be detected and quantitatively evaluated in addition to atomic absorption lines.

By adding a suitable molecule-forming reagent, molecular compounds are generated under optimized conditions. One or more molecular absorption bands in the spectral observation window can then be used for analytical evaluation and quantification of an analyte such as fluorine via CaF or GaF molecules. The graphite furnace technique allows very sensitive quantification with low sample and reagent volumes. This application note describes the procedure for the sensitive determination of low fluorine concentrations in the µg L^{-1} range using CaF or GaF molecule bands in drinking water samples.

The AS-GF autosampler automatically handles all required solutions such as modifiers, standards or samples and transfers them to the graphite furnace for measurement. The AS-GF autosampler and the graphite furnace technology allow fully automatic and software controlled intelligent or predefined dilution of the sample, application of the standard addition method, addition of defined amounts of standard to samples (spiking experiment) and preparation of a dilution series for calibration from a stock solution. With the graphite furnace technique there is no need for interference induced nebulization of the sample.

Materials and Methods

Reagents

- Certified fluorine stock solution (1000 mg L^{-1} F as NaF in water)
- Zr solution (10 g L^{-1} in diluted HCl)
- $Ga(NO_3)_3 \cdot xH_2O$ (99.999%), alternative: Ga standard solution (10 g L^{-1} in diluted HNO_3)
- $Pd(NO_3)_2$ matrix modifier (10 g L^{-1})
- $Mg(NO_3)_2$ matrix modifier (10 g L^{-1})
- Ba standard solution (1 g L^{-1} in diluted HNO_3)
- Ca standard solution (1 or 5 g L^{-1} in diluted HNO_3)
- Concentrated HNO_3 (62-65%, p.a.)
- Tergitol™ 15-S-9, substitute for TritonX-100™

Check the fluorine content of the reagents used, as this can greatly increase the blank value of the measurement. HF-stabilized solutions (e.g. Zr solution) are to be avoided. Reagents, samples and standards should not be stored or handled in containers made of fluorinated polymers (e.g. TPFE, PFA or MFA). Particular attention should be paid to the fluorine content of the reagent gallium or gallium nitrate. Fluorine contamination of this substance may vary between batches and manufacturers.

This application note presents three approaches for the determination of total fluorine by MAS. Method 1 is based on Ga-F absorption and is related to the research work of the Bundesanstalt für Materialforschung und -prüfung (BAM, Federal Institute for Materials Research and Testing) under the leadership of Mr. Meermann[1]. Method 2 is also based on Ga-F absorption and is related to the experience of Analytik Jena GmbH+Co. KG. The third method (method 3) is based on Ca-F absorption and is related to the research work of the University of Graz under the leadership of Mr. Feldmann[2].

The following list of methods presented allows the user to choose between different approaches and to use the most suitable one for his measuring task. The following reagents are required for the methods presented:

Used reagents

Method 1

- Zr solution (1 g L^{-1}) for graphite tube coating, diluted with ultra-pure water
- Modifier mix: Ga/Pd/Mg/Zr (1 g L^{-1} Ga, 0.5 g L^{-1} Pd, 0.5 g L^{-1} Mg, 0.5 g L^{-1} Zr), diluted with ultra-pure water
- 200 µg L^{-1} fluorine stock solution in 0.5% (v/v) HNO_3

Method 2

- Zr solution (1 g L^{-1}) for graphite tube coating, diluted with ultra-pure water
- Modifier mix: Pd/Mg/Zr (1 g L^{-1} Pd, 0.5 g L^{-1} Mg, 20 g L^{-1} Zr), diluted with ultra-pure water
- Ba modifier (10 mg L^{-1}), diluted with ultra-pure water
- Ga modifier (10 g L^{-1} Ga), diluted with ultra-pure water
- 200 µg L^{-1} fluorine stock solution in 0.5% (v/v) HNO_3

Method 3

- Zr solution (1 g L^{-1} in deionized water) for graphite tube coating
- Modifier: Ca standard solution (1 g L^{-1})
  Remark: The sensitivity and linear working range can be improved by increasing the Ca concentration of the modifier solution (e.g. to 5 g L^{-1} Ca). However, this will also cause the graphite tube to deteriorate more rapidly.
- 500 µg L^{-1} fluorine stock solution in 0.5% (v/v) HNO_3 (200 µg L^{-1} for method of additions)

Sample and sample preparation

Tap water: The water sample taken was stabilized with 0.5% (v/v) HNO_3 and analyzed without further preparation. Sample dilution can be performed fully automatically by the AS-GF autosampler. The dilution factors used for the series of measurements presented are given in Table 5; 0.5% v/v HNO_3 was used as diluent.

Rinsing solution

0.2 % (v/v) HNO_3 and 0.002 % (m/v) Tergitol™ 15-S-9 in deionized water.

Instrumentation

The device configuration and the method parameters are listed below (table 1 and 2). The temperature-time programs used for the methods presented are shown in table 3.

Before the actual measurement, the graphite tube was coated with zirconium. It is not necessary to repeat this procedure for each series of measurements. A new coating of the tube is recommended if the measured values decrease, or the repeatability deteriorates. For this process, 40 µL of a 1 g L^{-1} Zr solution were injected six times into the tube and dried in stages. An automated coating program of the operating software was used for this process.

Table 1: Instrument configuration and material

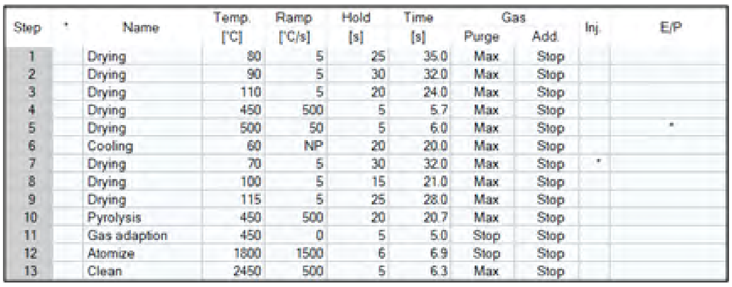
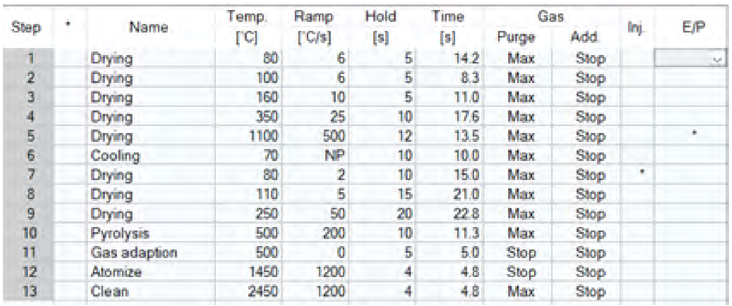
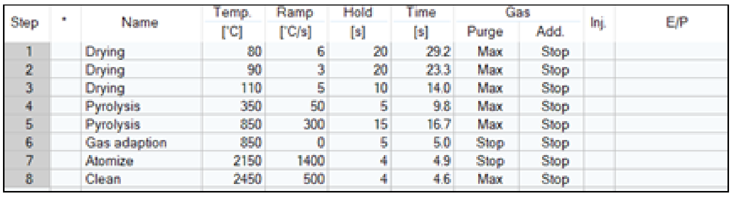
Parameter	Specification
Instrument	contrAA 800 G/D
Autosampler	AS-GF
Graphite tube type	PIN platform tube (Zr coated)
Injected volume of sample or standard	20 µL
Rinsing solution	0.5 % (v/v) HNO_3 and 0.05 (w/w) Tergitol 15-S-9

Table 2: Method settings and evaluation parameters

Method	Element (Molecule)	Wavelength [nm]	Number of. eval. pixels	Meas. time [s]	Modifier	Background correction
Method 1	F (GaF)	211.2480 211.5530	3	6.9	30 µL Ga/Pd/Mg/Zr* *Ga 1 g L^{-1}* *Pd, Mg, Zr 0.5 g L^{-1}*	IBC
Method 2	F (GaF)	211.2480 211.5530	3	4.8	5 µL Ga 10 g L^{-1}* 5 µL Pd/Mg/Zr* *Pd 1 g L^{-1}* *Mg 0.5 g L^{-1}* *Zr 20 mg L^{-1}* 5 µL Ba 10 mg L^{-1} 5 µL Ga 10 g L^{-1}	IBC
Method 3	F (CaF)	606.4337	7	4.9	10 µL Ca 1 g L^{-1}	IBC

IBC: Iterative baseline correction
*Thermal pre-treatment

Table 3: Temperature-time programs

Method	**Temperature-time program**
Method 1 (GaF)	
Method 2 (GaF)	
Method 3 (CaF)	

Method 1 (GaF)

Step	*	Name	Temp.	Ramp	Hold	Time	Gas		Inj.	E/P
			[°C]	[°C/s]	[s]	[s]	Purge	Add.		
1		Drying	80	5	25	35.0	Max	Stop		
2		Drying	90	5	30	32.0	Max	Stop		
3		Drying	110	5	20	24.0	Max	Stop		
4		Drying	450	500	5	5.7	Max	Stop		
5		Drying	500	50	5	6.0	Max	Stop		*
6		Cooling	60	NP	20	20.0	Max	Stop		
7		Drying	70	5	30	32.0	Max	Stop	*	
8		Drying	100	5	15	21.0	Max	Stop		
9		Drying	115	5	25	28.0	Max	Stop		
10		Pyrolysis	450	500	20	20.7	Max	Stop		
11		Gas adaption	450	0	5	5.0	Stop	Stop		
12		Atomize	1800	1500	6	6.9	Stop	Stop		
13		Clean	2450	500	5	6.3	Max	Stop		

Method 2 (GaF)

Step	*	Name	Temp.	Ramp	Hold	Time	Gas		Inj.	E/P
			[°C]	[°C/s]	[s]	[s]	Purge	Add.		
1		Drying	80	6	5	14.2	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		Cooling	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		Drying	250	50	20	22.8	Max	Stop		
10		Pyrolysis	500	200	10	11.3	Max	Stop		
11		Gas adaption	500	0	5	5.0	Stop	Stop		
12		Atomize	1450	1200	4	4.8	Stop	Stop		
13		Clean	2450	1200	4	4.8	Max	Stop		

Method 3 (CaF)

Step	*	Name	Temp.	Ramp	Hold	Time	Gas		Inj.	E/P
			[°C]	[°C/s]	[s]	[s]	Purge	Add.		
1		Drying	80	6	20	29.2	Max	Stop		
2		Drying	90	3	20	23.3	Max	Stop		
3		Drying	110	5	10	14.0	Max	Stop		
4		Pyrolysis	350	50	5	9.8	Max	Stop		
5		Pyrolysis	850	300	15	16.7	Max	Stop		
6		Gas adaption	850	0	5	5.0	Stop	Stop		
7		Atomize	2150	1400	4	4.9	Stop	Stop		
8		Clean	2450	500	4	4.6	Max	Stop		

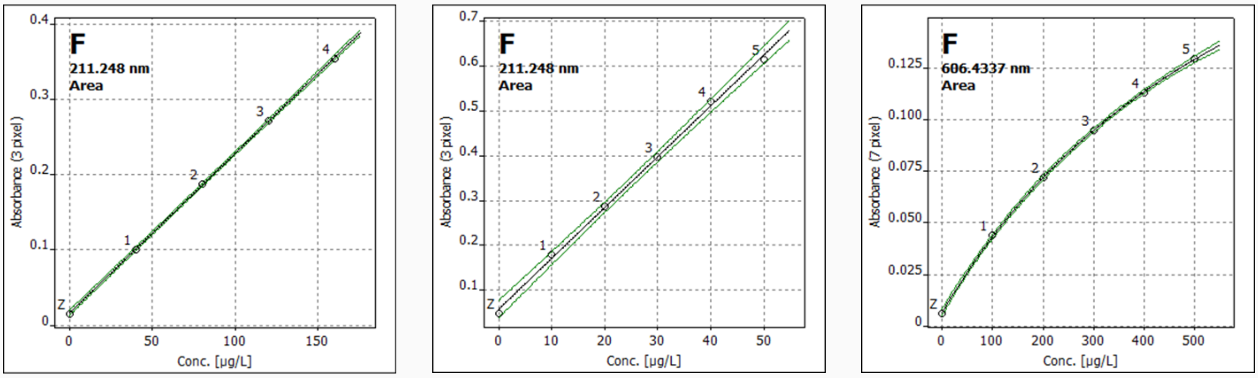
Calibration

The needed dilution steps for system calibration (standard calibration and method of addition) can be automatically prepared by the AS-GF autosampler. The concentrations of the calibration standards used are listed in table 4. Typical calibration functions of the methods presented are shown in figure 1.

For standard calibration a stock solution was gradually diluted with 0.5 % (v/v) HNO_3. The injection volume of standards or sample was 20 µL. The standard addition procedure was additionally used for method 3 (CaF). For this approach, an injection volume of 12 µL each was used for sample and added standard solution.

Table 4: Concentrations of the calibration standards

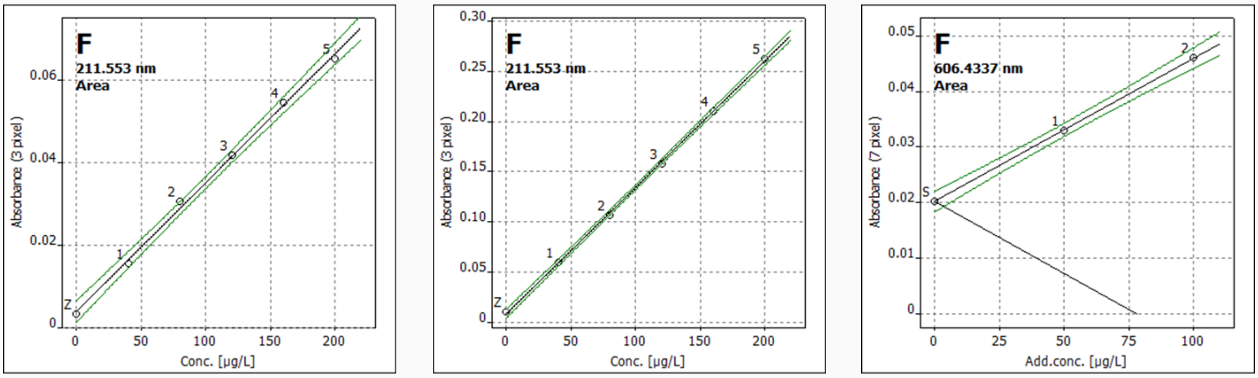
Standard	**Fluorine concentration [µg L^{-1}]**					
	Method 1 (GaF)		**Method 2 (GaF)**		**Method 3 (CaF)**	
	211.248 nm	**211.553 nm**	**211.248 nm**	**211.553 nm**	**Std. calib.**	**Meth. of add.**
Stock solution	200	-	50	200	500	200
Cal. 0	0	0	0	0	0	Sample
Std. 1	40	40	10	40	100	+ 50
Std. 2	80	80	20	80	200	+ 100
Std. 3	120	120	30	120	300	
Std. 4	160	160	40	160	400	
Std. 5	-	200	50	200	500	



Method 1 (GaF),
F211.248 – linear, R^2(adj.)=0.9998

Method 2 (GaF),
F211.248 – linear, R^2(adj.)=0.998

Method 3 (CaF)
Std.calib.: nonlinear, R^2(adj.)=0.9998



Method 1 (GaF),
F211.553 – linear, R^2(adj.)=0.997

Method 2 (GaF),
F211.553 – linear, R^2(adj.)=0.9993

Method 3 (CaF),
Method of add.: linear, R^2(adj.)=0.9990

Figure 1: Calibration functions

Results and Discussion

The measurement results for the tap water sample using the different methods are given in table 5.
The value for fluoride in water is given as 0.10-0.18 mg L^{-1} by the regional supplier (year of data collection 2024[3]). The reported limits of detection and quantification (LOD/LOQ) were determined by the blank value method (3σ or 9σ blank value criterion). To estimate the matrix influence on the fluorine determination by MAS (non-spectral interference), fluorine concentrations in the calibration range were automatically spiked into the samples. The recovery rates of the spiking performed are also given in table 5.

The high affinity of fluorine for gallium is also reflected in the recovery rates (RR, 94-100%) determined in these test series. For sample type drinking water, no matrix effect could be detected in these analytical methods. The RR for method 3 (CaF) was 78%, indicating a matrix influence of the measurement between the sample type and the standards used. The quantification of the fluorine content using the method of addition resulted in a 127% higher content in the tested water sample. This value is comparable to the results obtained with methods 1 and 2 (GaF)[3].

In summary, the following should be noted: Method 3 (CaF) offers a simple methodology and can be easily adapted to other sample types. A matrix influence by the sample type must be checked with this approach. Methods 1 and 2 are more robust to matrix effects. Compared to the CaF method, these methods require a higher preparative effort. The required sample preparation and liquid handling can be fully automatically performed with the contrAA 800 G/D.

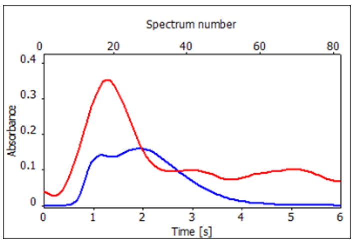
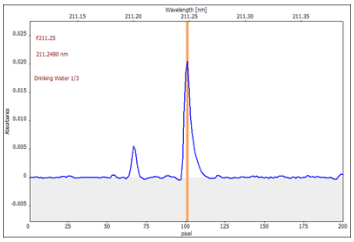
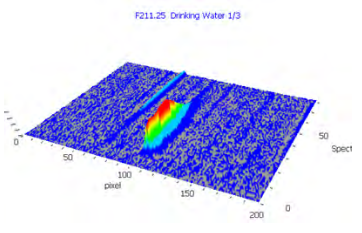
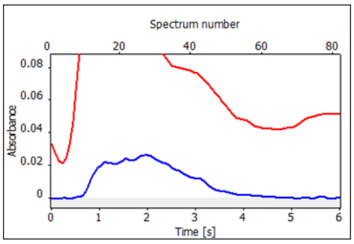
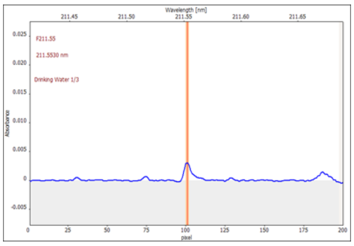
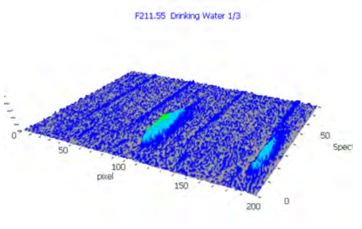
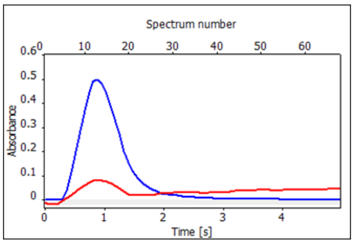
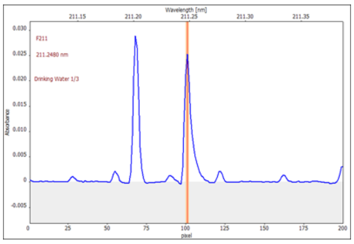
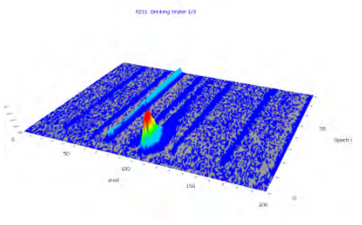
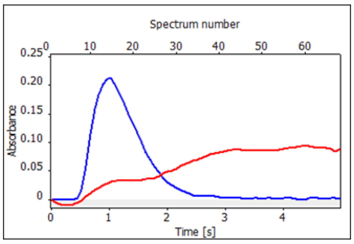
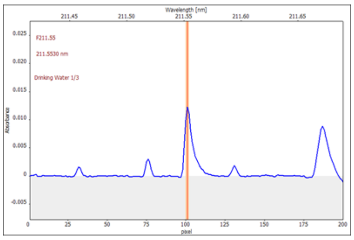
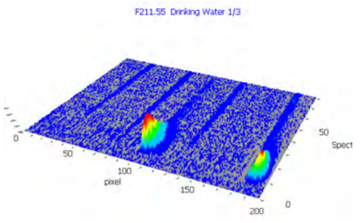
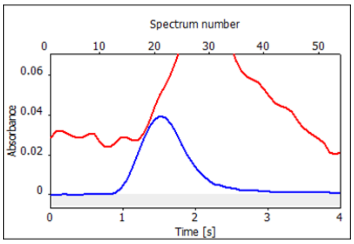
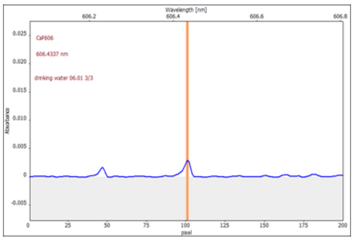
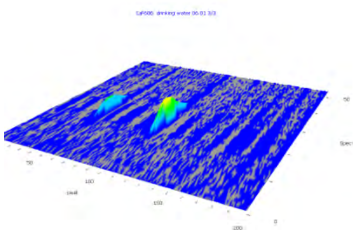
The characteristic signals and spectra of the molecular bands resulting from the analysis of the samples are shown in table 6. Due to the special and unique design of the contrAA 800, the spectral environment of the analysis line can be recorded, evaluated and adjusted in addition to the classic evaluation of the signals. The spectrum obtained from the measurements shows a Ga absorption line at 211.2480 nm in addition to the selected GaF band. Another GaF band at 211.5530 nm in addition to the selected GaF absorption peak is visible. Additional absorption bands of the molecules are also visible for the CaF method in the spectral observation range at 606.4337 nm. These mentioned and other recognizable absorption bands have no direct overlap with the selected evaluation range. Therefore, no spectral correction needs to be applied.

Table 5: Results for the drinking water sample, QC spike recovery, and obtained LOD/LOQ values

Method	**Line [nm]**	**Dilution factor**	**Measured value ± SD [µg L^{-1}]**	**RR of a spiked concentration [%]**	**LOD [µg L^{-1}]**	**LOQ [µg L^{-1}]**
Method 1 (GaF)	211.2480	1	148.0 ± 1.8	94	0.89	2.7
	211.5530	1	150.8 ± 2.9	98	6.0	18
Method 2 (GaF) Std. calibr.	211.2480		150.3 ± 1.3	104	0.52	1.6
	211.5530	1	152.6 ± 1.3	97	1.9	5.6
Method 3 (CaF) Std. calibr.	606.4337	1	122.6 ± 0.96	78	6.5	20
Method 3 (CaF) M. of add.	606.4337	2	156.1 ± 0.65*	-	-	-

SD: Standard deviation
RR: recovery rate
LOD/LOQ: Limit of detection/quantification (determined by 3σ/9σ criterion)
*Error is based on the standard deviation of the method.

Table 6: Characteristic spectra and spectral vicinity of fluorine molecule bands in the drinking water sample

Method/Line	Signal	2D spectrum	3D plot
Method 1 211.248 nm (GaF)			
Method 1 211.553 nm (GaF)			
Method 2 211.248 nm (GaF)			
Method 2 211.553 nm (GaF)			
Method 3 606.434 nm (CaF)			

blue: analyte signal; red: background signal

Summary

The HR-CS graphite furnace AAS contrAA 800 G/D provides high performance total fluorine analysis. Convenient and automatic sample handling is provided by the AS-GF autosampler.

This document describes basic method approaches and achievable detection limits for aqueous samples. High sensitivity and reliable recovery rates demonstrate the analytical capabilities of the HR-CS MAS technique for the detection and quantification of fluorine under optimized conditions.

In this application note, drinking water has been selected as an exemplary sample type. The applicability of this method to other matrices needs to be tested. Important factors are the solubility of the reagents used in the sample matrix and their influence on molecule formation. The MAS approach to fluorine determination is part of ongoing research and further applications for this exciting and unique method will undoubtedly be developed in the future.

Figure 2: contrAA 800 G/D with AS-GF autosampler

Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
contrAA 800 G	815-08001-2	HR-CS AAS for graphite furnace techniques
contrAA 800 D	815-08002-2	HR-CS AAS for flame- and graphite furnace techniques
Graphite tube with PIN platform	407-A81.025	Graphite tube with PIN-platform, pyrolytically coated (10 pcs)
Sample vials 5 mL	407-230.073	PP-sample vials, 5 mL (10 pcs)
Sample vials 1.5 mL	407-218.852	Polystyrene-sample vials 1.5 mL (1000 pcs)

References

[1] An optimized Methode for PFAS analysis using HR–CS–GFMAS via GaF detection, Fabian Simon, Marcus von der Au, Lennart Gehrenkemper, Björn Meermann, Talanta 281 (2025)

[2] The use of high resolution graphite furnace molecular absorption spectrometry (HR -MAS) for total fluorine determination in extractable organofluorines (EOF) Abdullah Akhdhar, Mauana Schneider, Alice Orme, Lara Schultes, Andrea Raab, Eva M. Krupp, Jonathan P. Benskin, Bernhard Welz, Jörg Feldmann, Talanta 209 (2020)

[3] https://www.jenawasser.de/

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