Fluorine Detection in Drinking Water Using HR-CS AAS

Due to its high electro negativity the element fluorine is the most reactive non-metal and thus does not occur in elementary, but only in combined form. Fluorine is the most widespread halogen. Its share in the earth's crust is approx. 0.08%. It occurs in large quantities in apatite $Ca_5(PO_4)_3(OH,F)$ and in fluorite CaF_2 as well as in the almost exhausted cryolite Na_3AlF_6 [1]. It is therefore no surprise that fluoride is also found in almost all water bodies - although the fluoride concentration can differ greatly by water type and the geogenic conditions. Seawater contains more than 1mg/L fluoride, rivers and lakes approx. 0.05 - 0.5mg/L, whereas in ground water values above 0.5mg/L are relatively rare. However, in deepwater, especially in sources from hydrothermal deposits, significantly higher fluoride content can also be found, e.g. in geysers more than 20mg/L. Mainly responsible for the fluoride content are the pH value, temperature, solubility conditions and geological preconditions [2, 3].

There are two sides to the effects of fluoride on human health. On the one hand it is essential for the human organism, because the fluoride ingested with food is a condition for the mineralisation of the apatite in bones and teeth. In this respect a corresponding fluoride content in the drinking water as the most important food is also of great importance with regard to an adequate caries prophylaxis. On the other hand too high a daily absorption of fluoride in all the ingested food can have fatal consequences. Tooth and bone fluorosis result if the daily total fluorine absorption exceeds approximately 20mg F/day [4].

The control of the fluoride concentration in our foodstuffs is therefore of major importance. Drinking water is the number 1 food and thus subject to a particularly intensive control. Fluoride has been categorised as a substance causing health disorders after a given concentration. The limit defined for fluoride in the drinking water regulations is 1.5mg/L [5].

MEASURING METHODS FOR FLUORIDE DETECTION

The detection of fluorine as non-metal has been sufficiently described in the literature. The methods range from classical gravimetry and volumetry to photometry and electrochemical titration. The methods for detecting the fluoride concentration in water dominating today are the ion chromatography (IC) [6] and the use of ion-selective electrodes (ISE) [7]. Both detection methods have in common that they only respond to ionic dissolved fluoride. Organic or covalent combined fluorine is not detected, so that these detection methods can only be used for purely water-based matrixes.

SPECTROSCOPIC METHODS

Spectroscopic methods, such as ICP-OES, for the detection of fluorine are not practicable because of the very high ionisation potential of 17.42 eV and the resonance lines of the fluorine thus being below 100nm. For a similar reason, classic AAS can also not be used to determine fluorine. A suitable alternative is the detection of fluorine using molecular absorption spectrometry (MAS). First investigations were carried out by Dittrich [8,9] and Tusunda [10], roughly at the same time. Due to the relatively moderate resolution of the spectrometers used at the time and a limited background correction, this method did not succeed in the detection of fluorine.

With the development of the High-Resolution Continuum Source AAS (HR-CS AAS) and the commercial availability of these AAS devices with the contrAA 300 and contrAA 700 from Analytik Jena the conditions have now been provided to use this method successfully in the detection of fluorine.

Below a simple, fast and robust method for the detection of fluorine in drinking water using HR-CS AAS is described and its practical applicability tested in different drinking water samples and a reference material.

FLUORINE DETECTION BY MOLECULAR ABSORPTION WITH HR-CS AAS

In recent years, based on the availability of HR-CS AAS, various methods for the detection of non-metals such as P, S, F, Cl, Br, J by molecular absorption in combination with an AAS were published. An article by Welz et.al. [11] providing an overview summarised the work.

The analytical use of molecular absorption spectrometry for the detection of fluorine is based on the formation of stable monofluorides (AlF, GaF, InF, CaF). These biatomic molecules can just like atoms absorb defined energy from a continually emitting spectral radiation source, resulting in the generation of molecular absorption spectra. The molecular absorption spectra correspond to the molecular transitions between the different molecule states.

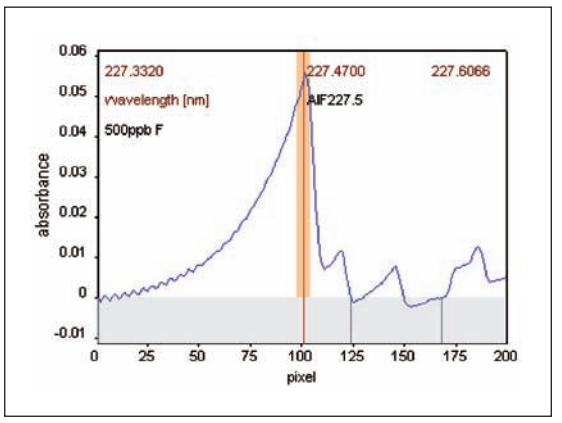

Figure 1. Molecular absorption spectrum of AlF by wavelength resolution in the region of 227.47nm, injection of 10ng F

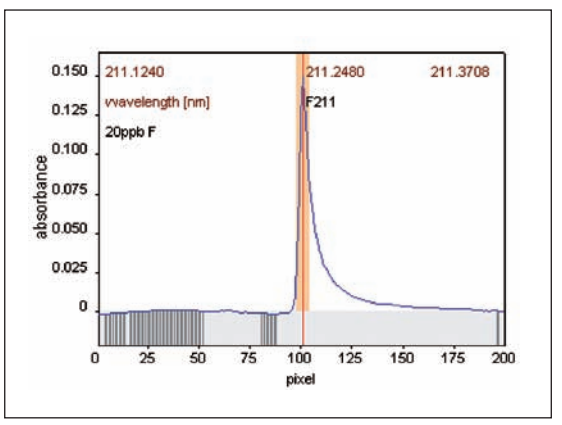

Figure 2. Molecular absorption spectrum of GaF by wavelength resolution in the region of 211.248nm, injection of 10ng F

A difference is made between electron excitation, oscillation and rotation transitions. The number of possible transitions is greater than for atoms, which means that the molecular absorption spectra have more lines than atomic absorption spectra. The line width of various molecular absorption lines is roughly equal to that of atomic absorption lines and can thus be resolved and used for analysis in the HR-CS AAS.

Figures 1 and 2 show the molecular absorption spectra of the most sensitive AlF and GaF molecule lines. All subsequent investigations were carried out on the molecular absorption line of GaF at a wavelength of 211.248nm due to its greater sensitivity and better resolved molecular lines.

EXPERIMENTAL

Instrumentation

All measurements were carried out with a HR-CS AAS contrAA® 700 *(Figure 3)* from Analytik Jena using graphite furnace technology.

This is an atomic absorption spectrometer with a Xe short arc lamp as radiation source [12,13]. The Xe lamp emits a continuous spectrum in the range of 185 - 900nm. This provides every wavelength required for analytical use. This is a condition for the analytical use of molecular absorptions of any wavelength. As atomisers a flame and a transversely heated graphite tube furnace are available in two separate rooms. The high resolution spectrometer consists of a prism upstream monochromator and an echelle grating to guarantee a resolution of 2pm at a wavelength of 200nm. As detector an CCD array is used guaranteeing a simultaneous and powerful background correction and providing additional information about the examined analysis line through the simultaneous evaluation of 200 detector pixels [14].

> ***"The methods range from classical gravimetry and volumetry to photometry and electrochemical titration."***

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Figure 3. HR-CS AAS contrAA® 700 (Analytik Jena)

Method optimisation of the GaF molecular absorption

The temperature/time program for the analytical use of molecular absorption consists of 3 phases: Drying, ashing and molecule formation. During the drying and ashing steps any advance losses of the analyte in the form of volatile HF must be prevented by optimising the drying and pyrolysis temperature and using an efficient modifier. The purpose of the molecule formation phase is to generate the desired biatomic molecule by adding an appropriate molecule generation reagent. By selecting an optimal temperature a sufficient large number of these molecules must be formed. However, the temperature must not be chosen too high to prevent too early a decomposition into its atomic components.

To form Ga monofluoride a 10g/L Ga standard (from SCP Science) in 4% HNO3 is used as molecule formation reagent. The best analytical results could be achieved when the graphite furnace with integrated PIN platform used was permanently coated with Zr before its analytical use. To stabilise the analyte and the Ga during ashing, a Pd/ Zr modifier (0.1% Pd, 20mg/L Zr) was brought into a thermally active form together with the molecule formation reagent at 1100°C before each sample injection. Under these conditions an ideal ashing temperature of 550°C was identified. NaAc and Ru-III-nitosyl nitrate were used as modifier to reduce advance analyte losses by formation of volatile HF. Under these conditions 1550°C was identified as the ideal molecule formation temperature.

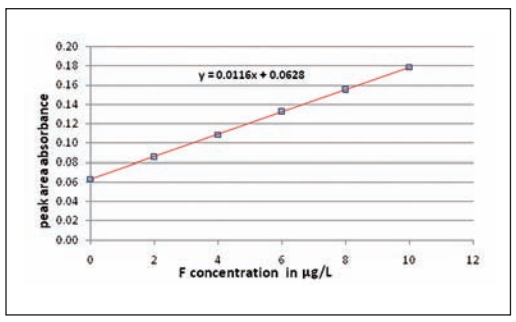

Figure 4. F calibration curve using GaF molecular absorption at a wavelength of 211.248nm: 2 – 10µg/L F, 20µL sample injection

Calibration

Under the ideal conditions established a calibration was carried out in the range of 2 - 10 µg/L F *(Figure 4)*. On the basis of this calibration and the triple standard deviation from 11 repetitions of the blank calibration value a detection limit of 0.26µg/L F was determined. This detection limit for fluorine is approx. one decade better than with IC or ISE.

To test the developed method 3 drinking water samples, one mineral water and two certified reference materials were examined. Because the fluoride content to be expected was way beyond the calculated detection limit, another calibration was carried out in the range of 10 - 50 µg/L F.

The results of the examined samples are shown in *Table 1* and display a very good correspondence to the certified values, the parallel determinations using ISE and the average manufacturer information in the case of the mineral water.

SUMMARY

A simple, fast, fully automatable and robust method for the detection of fluorine in drinking water is presented. The method is based on the measurement of molecular absorption of GaF at a wavelength of 211.248 nm with a commercially available HR-CS AAS in graphite furnace technology. As molecule formation reagent a 10 g/L Ga solution is used. The best results were achieved with a permanently Zr coated PIN platform tube. To stabilise the analyte and to prevent advance losses various modifiers are used. Using a special thermal pre-treatment of the Pd/ Zr modifier and a reagent at 1100°C fluorine can be pyrolysed up to 550°C and is available at 1550°C for an efficient molecule formation. Using this optimised method a detection limit of 0.26µg/L F was identified which is clearly greater than that of all other currently available methods. With the basic principle of molecular absorption (MAS) analogue to atomic absorption (AAS) the detection is very robust. Limitations and disadvantages of the common methods IC (sample throughput, limitation to water-based medium, non-particular samples) and ISE (limited pH range, defined ionic strength, salt content) are not a factor. Another benefit of this method is that the range of application can also be extended to biological matrixes, such as urine, serum and blood, without difficulty.

Thus for the first time a simple method for the detection of the total fluorine content (ionic and covalent combined fluorine) exists. Time-consuming and error-prone upstream pyrohydrolysis or derivatisation for water-based media become obsolete. Even fluorine in only partially hydrolised, yet water-based combinations, such as in sodium monofluorphosphate (MEP), a caries prophylactic active component in toothpaste, is detected completely using the method described. This simplifies and shortens the quality control during production for the detection of the total fluorine content in toothpaste. Other potential applications can be found not least by the detection of the total fluorine after the digestion of solid samples.

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*Table 1. Sample results, *VF= dilution factor, ** information value, *** concentration information from the manufacturer catalogue*

Sample	VF*	Concentration in µg/L F	RSDin %	ISE concentration in mg/L F	Certified concentration in mg/L F
ION-915	1	41,0 ± 2,0	2,4		0,03**/0,048***
Hamilton-20	10	424 ± 21	2,5		0,42 ± 0,078
TW Bad Berka	5	132 ± 8,7	4,3	0.14	
TW Tiefengruben	5	146 ± 8,8	2,8	0.15	
TW Sachsenhausen	5	237 ± 11	1,1	0.25	
Mineral water	5	148 ± 8,2	1.5	0.16**	
QC standard 4:		38.7 ± 1.14			
			0.4		
40µg/L F		(96,7%)			
QC standard 2:		20.4 ± 1,03			
			3.7		
20µg/L F		(102%)			