# Method Development for the Determination of Fluorine in Water Samples via Molecular Absorption of CaF Using A High-Resolution Continuum Source Electrothermal Atomic Absorption Spectrophotometer

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**Abstract.** In this study, determination of fluorine in water samples was established via the rotational fine structured molecular absorption of calcium mono-fluoride (CaF) at 606.440 nm using a high-resolution continuum source electrothermal atomic absorption spectrophotometer. To generate CaF in the gas phase of graphite furnace, samples were pipetted together with calcium as its nitrate form. The effect of amount of calcium, graphite furnace program, coating the graphite tube and platform with Zr and Ir and the use of modifier (Pd, Mg and Pd+Mg) on the sensitivity and linearity were investigated. In the presence of 40 µg of Ca, a perfect linearity up to 0.1 µg of F was maintained applying a pyrolysis temperature of 700ºC and a molecule forming temperature of 2250ºC in pyrolytically coated platforms. The limit of detection and characteristic mass of the method were 0.21 ng and 0.13 ng of F, respectively.

**Key words:** High-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS-ETAAS); Molecular absorption spectrometry (MAS); Fluorine determination; Calcium monofluoride (CaF); Water samples

## Introduction

Fluorine is an essential element trace element for human health, but exposure of fluorine in excess amounts may cause dental and/or skeletal fluorosis (Wang et al., 2004). Even though absence of fluorine does not cause dental caries, ingestion of fluorine may help to reduce tooth decay. The effect of fluorine depends on its total daily intake from all sources. Drinking water is typically the largest source for fluorine; other methods of fluorine therapy include fluoridation of toothpaste, salt, and milk (Petersen et al., 2004). Since the amount of fluorine intake is important, fluorine contents of water, beverages and many food and drink samples have been investigated deeply in literature, which were well reviewed by Huang et al.(2006).

Atomic absorption spectrometry (AAS) is a traditional analytical method for quantitative determination of trace metals and metalloids. The traditional line source atomic absorption spectrometry cannot be used for determination of fluorine because the main resonance line of F is located at 95 nm which cannot be instrumentally applied. With the new generation high resolution continuum source atomic absorption spectrometer (HR-CS-AAS), it is possible to determine fluorine with any suitable diatomic molecule formed with a selected metal at its any appropriate rotational hyperfine rotational absorption wavelength. There are limited number of studies on the determination of fluorine by HR-CS-AAS using molecular absorption by several diatomic molecules like AlF (Ozbek and Akman, 2012), GaF (Gleisner et al., 2010), CaF (Mores et al., 2011) and SrF (Ozbek and Akman, 2012).

This study describes a new method for determination of fluorine in water matrix by HR-CS-ETAAS using molecular absorption line of CaF. The experimental parameters were optimized and method was validated.

## Materials and Methods

A graphite furnace atomic absorption spectrophotometer Analytik Jena ContrAA 700 high-resolution continuum source atomic absorption

spectrophotometer equipped with MPE auto sampler (Analytik Jena, Jena, Germany) and a 300W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) operating in a hot-spot mode as a continuum radiation source was used for all measurements. The equipment presents a compact high-resolution double echelle monochromator and a charge-coupled device (CCD) array detector with a resolution of about 5 pm per pixel. Measurements were carried out at 606.440 nm molecular absorption line of CaF with 3 pixels (central pixel±1). All measurements were performed using pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025).

In all dilutions a high-purity water (resistivity 18.2 $M\Omega.cm$) obtained by a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungsysteme GmbH, Niederelbert Germany) was used. Inorganic acids and reagents were of analytical grade ($HNO_3$, 65% (v/v), Merck, Darmstad, Germany). The fluorine standard was prepared from sodium fluoride (Merck, Darmstad, Germany). A stock solution of 10000 mg $L^{-1}$ calcium as molecule forming agent was prepared from barium nitrate (Merck, Darmstadt, Germany). The waste water standard reference material SPS-NUTR-WW2 was provided from LGC Standards (Middlesex, England). Drinking and tap water samples had obtained from different cities of Turkey.

Determination of fluorine was performed using the rotational molecular absorption line of diatomic CaF at 606.440 nm by HR-CS-AAS. Samples (or standard solutions) and 4000 $\mu g$ $L^{-1}$ of calcium as the nitrate were pipetted as 10 $\mu L$.

## Results and Discussion

### Choice of molecule-forming reagent

Since the method is based on the measurement of the molecular absorption of a diatomic molecule formed between the analyte with a selected element at one of its finely structured rotational lines, it is very important to choose the appropriate molecule. Diatomic molecule of F formed should be stable in gas phase. The diatomic species with bond dissociation energies above 500 kJ $mol^{-1}$ are suitable for this purpose. Moreover, the molecular absorption sensitivity of the working wavelength for the diatomic molecule should be high enough to detect small F concentrations. It was expected that calcium would be an appropriate element for this purpose as well.

The 3D (i.e., time and wavelength-resolved) absorption spectra obtained for water sample spiked with 10 $\mu g$ $L^{-1}$ F in the vicinity of the molecular absorption peak of CaF at 606.440 nm is depicted in Figure 1. The background is low, and the MAS of CaF is smooth. There is no spectral overlap from the matrix. Therefore, all determinations of F throughout this study were performed using the rotational molecular absorption line of CaF at 606.440 nm.
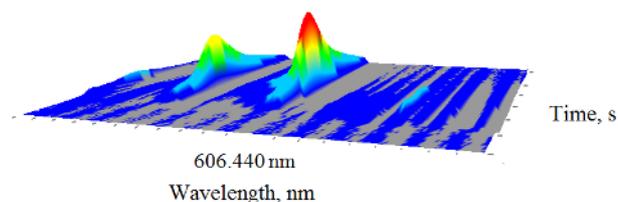


**Fig. 1.** Time and wavelength resolved absorption (3D) spectra obtained for water sample spiked with 10 $\mu g$ $L^{-1}$ in the vicinity of 606.440 nm molecular absorption peak of CaF. Ca: 4 mg $mL^{-1}$.

### Optimization of graphite furnace program

The graphite furnace program used for determination of F from the MAS of CaF at 606.440 nm should be designed to combine Ca and F while removing certain matrix consitituents that may cause interferences and forming CaF. The maximum sensitivity is obtained with 700°C pyrolysis temperature with a molecule forming temperature 2250°C.

### Use of modifiers

In this study, the effects of Pd, Pd+Mg, Ir and Zr modifiers on the sensitivities and pyrolysis and atomization temperatures were investigated. When Pd or Pd+Mg modifiers were used in the graphite furnace, no significant improvement was observed. In contrast, the sensitivities were reduced.

### Optimization of the amount of calcium

The amount of calcium should be high enough to produce constant and maximum CaF sensitivity for all F concentrations in the matrix of the sample. In this case, CaF concentration and its absorbance would linearly be proportional with F concentration. Otherwise, non-linear relationship between F and CaF concentrations occurs which is the case in some applications. The absorbances for CaF in water samples linearly increased up to 20 $\mu g$ (10 $\mu L$ of 2000 mg $L^{-1}$) of Ca and remained almost constant at higher Ca concentrations. In this study, being on the safe side, 40 $\mu g$ of Ca was used as the molecule forming element for all determinations.

### Linearity

The sensitivities and linearities of working curves for F obtained from the MAS of CaF at 606.440 nm were investigated in the presence of 40 $\mu g$ of Ca. The perfect linearity was obtained up to 10 mg $L^{-1}$ of F which was expected to be much higher than F concentrations in samples. On the other hand, in complex matrices, Ca and F interact not only with each other but also with the other constituents. In this case, concentration of CaF formed will not be the same with that in standard solutions. In this case, to eliminate the non-spectral interferences, standard addition technique seems to be more appropriate

**Table 1.** Fluorine concentrations[1] in drinking water, tap water and certified reference samples found by linear calibration and standard addition techniques via molecular absorption of CaF at 606.404 nm. Ca: 4 mg mL$^{-1}$; N=3.

| Sample | Expected Value[2] ($\mu$g mL$^{-1}$) | Value Found by Linear Calibration ($\mu$g mL$^{-1}$) | Value Found by Standard Addition ($\mu$g mL$^{-1}$) |
|---|---|---|---|
| Waste water (SPS-NUTR WW2) | 10.00±0.10 | 9.80±0.06 | 9.70±0.06 |
| Bottled Drinking Water 1 | 0.01 | <LOD | <LOD |
| Bottled Drinking Water 2 | 0.25 | 0.23±0.01 | 0.24±0.05 |
| Tap Water Sample 1 | NG[3] | 0.59±0.06 | 0.60±0.03 |
| Tap Water Sample 2 | NG[3] | 0.87±0.04 | 0.85±0.04 |
| Tap Water Sample 3 | NG[3] | 0.41±0.03 | 0.40±0.08 |
| Tap Water Sample 4 | NG[3] | 0.28±0.02 | 0.25±0.06 |
| Tap Water Sample 5 | NG[3] | 0.75±0.06 | 0.77±0.03 |
| Tap Water Sample 6 | NG[3] | 0.63±0.04 | 0.65±0.04 |

[1] Results presented are mean ± standard deviation (N=3).
[2] The fluoride concentrations given on the bottle of water sample or certified value of CRM
[3] NG: not given

technique for quantifications of F in real samples. However, the results in real water samples found by linear calibration and standard addition techniques were not significantly different. This shows that the above-mentioned problems (non-spectral interferences) did not occur in the determination of F in water samples which can be attributed to the simple matrices of the samples.

*Figures of merit*

In general, limit of detection (LOD) is calculated according to 3 times the standard deviation ($\sigma$) for 10 repetitive pipettings of the blank to the furnace ($3\sigma$ /slope of calibration graph) whereas the characteristic mass is calculated as the concentration of F corresponding to 0.0044 A i.e. 0.0044/slope of calibration graph. However, the standard deviations as well as the sensitivities may show some small discrepancies from day to day. In addition, the sensitivity and thus LOD and characteristic mass values depend on the amount of Ca as well. In this study, in order to determine LOD, 3 times the standard deviation for 10 repetitive pipettings of 10 $\mu$L of 4000 mg L$^{-1}$ of Ca with a water sample containing one of the lowest analyte content. The average LOD and the characteristic mass values found on various days were 0.21 ng and 0.13 ng (or 0.021 $\mu$g mL$^{-1}$ and 0.013 $\mu$g mL$^{-1}$ for 10 $\mu$L of pipetting), respectively. The accuracy of the method was tested using a certified reference waste water sample (SPS-NUTR-WW2). The results were in good agreement with certified values as well as the precision was satisfactory (RSD<15%). Finally, F contents of several water samples were determined linear calibration technique and standard addition technique.

**Conclusion**

A novel method is proposed for the determination of fluorine in different water samples using HR-CS-ET AAS via the MAS of calcium monofluoride formed in gas phase. In this method, there was no need to use modifiers or to cover the tubes and platform with Zr or Ir. Validation of method was performed with wastewater CRM and fluorine concentrations could be determined in the uncertainty limits of the certified value. The results in CRM and real samples obtained by linear calibration technique and standard addition were nearly similar but to be on safe side, it is advised to apply the standard addition technique for any quantification.

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