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Determination of fluorine in plant material via calcium mono-fluoride using high-resolution graphite furnace molecular absorption spectrometry with direct solid sample introduction

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A method has been developed for the determination of fluorine in plant materials using high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS) and direct solid sample analysis with calibration against aqueous standard solutions. The diatomic molecule CaF has been selected as the target molecule as it has been considered to provide more favorable conditions for this application compared to other diatomic molecules described in the literature. Using only 15 µg Ca as the molecule-forming reagent, it was possible using a pyrolysis temperature of 900 ºC and a vaporization temperature of 2000 ºC, values that are distinctly different from published values, and to obtain a much better sensitivity (m_0 = 44 pg) and limit of detection (36 pg absolute or 0.36 µg g^{-1} in the solid samples) compared to values published using the same target molecule. Two certified reference materials have been analyzed to confirm the accuracy of the proposed method. Several plant materials have been analyzed to confirm the applicability of the method to real samples; the concentrations were found to be between 2.7 and 29 µg g^{-1} F. It is obvious that HR-CS GF MAS is a new technique, which is not yet well explored, and which will require a lot more research to be well understood.

1. Introduction

Among the air pollutants, fluorine stands out due to its high phytotoxic potential. An excess of fluorine in vegetation can cause leaf damage, affect plant growth and result in public health problems. Fluorine is usually present in soils in the form of minerals such as fluorite (CaF_2), fluoroapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6).[1] In the case of anthropogenic sources, the presence of fluorine in the atmosphere is related to activities of heating of rocks, incineration of coal, casting of aluminum, production of superphosphate (from the apatite) and other mineral fertilizers.[2-4]

On the other hand, fluorine is also an essential element for humans. Its beneficial action in the prevention of dental caries was discussed controversially for many years, but is generally accepted nowadays. Because of its importance for human health, fluorides are for example added to drinking water and toothpaste; however, too much fluoride can also result in fluorosis. Excessive consumption of tea with high levels of fluoride, for example, increases the risk of dental fluorosis, particularly in countries where the water is already enriched with this element.[5,6] The occurrence of this disease was for example documented in China, where tea is a very popular beverage, and often consumed all day long.[7,8] For these reasons fluorine has to be determined routinely in a great variety of samples.[9-12]

Several analytical techniques have been developed and described for fluorine determinations including fluorimetry,[13-15] fluoride ion-selective electrodes,[12,16,17] ion chromatography,[18,19] and gas chromatography.[20] Details about these techniques for the determination of halogens in bioanalytical sciences were published in a recent review article.[21] Non-metals, such as fluorine, cannot be determined by atomic absorption spectrometry (AAS), because these elements are difficult to atomize and their absorption lines are in the vacuum ultraviolet region of the electromagnetic spectrum, which is not accessible with this technique.[22] However, with the introduction of commercially available equipment for high-resolution continuum source atomic absorption

spectrometry (HR-CS AAS), it became possible to determine non-metals, such as fluorine, using the electron excitation spectra of suitable diatomic molecules, which can be found in the UV and visible range of the electromagnetic spectrum, and exhibit a pronounced rotational fine structure.[22,23] One of the main advantages of using HR-CS AAS equipment for molecular absorption spectrometry (MAS) is the high resolution provided by the double monochromator with a prism for pre-dispersion and an echelle grating for high resolution that almost completely resolves the fine structure of the molecular bands, avoiding at the same time spectral interference and background correction errors.[24-26] In order to obtain the best sensitivity using MAS for the indirect determination of non-metals, it is necessary to optimize conditions to promote formation of the target diatomic molecule. It is desirable to choose a molecule with a bond strength greater than 500 kJ mol^{-1} to ensure its stability at elevated temperatures.[22]

The determination of fluorine using HR-CS MAS was for the first time reported by Huang et al.[27] using the absorption of the GaF molecule at 211.248 nm in an air-acetylene flame; they analyzed a super-phosphate certified reference material (CRM) to verify the accuracy of the method. Heitmann et al.[28] used the same molecule and wavelength for the determination of F in a zinc ore CRM and a single cell protein CRM in a graphite furnace (GF). Gleisner et al.[29] tried to optimize the determination of F by HR-CS GF MAS of the GaF molecule by adding various modifiers, which resulted in increased sensitivity and robustness, however at the expense of a more complex procedure, which required a change in the software. These authors determined F in various natural and mineral water samples, and later also in toothpaste.[30] Krüger et al.[31] succeeded to quantify the fluorine-containing drug 5-fluorouracil in cancer cells also using the absorption of the GaF molecule in a GF. Qin et al.[32] used an off-line coupling of reverse-phase liquid chromatography to HR-CS GF MAS for the identification and quantification of fluorinated organic compounds in environmental and biological samples.

In most of the early applications of HR-CS MAS for the determination of fluorine, GaF was preferred as the target molecule over AlF because of the narrower profile of the GaF band head at 211.248 nm, its relative freedom from spectral interference and its high sensitivity. However, this high sensitivity also caused problems due to increased blank values, so that other molecules were investigated as well more recently. Bücker and Acker[33] used the absorption of the AlF molecule at 227.460 nm for the determination of F in process etching solutions of the photovoltaic industry in a GF and barium as a modifier. Ozbek and Akman[34] also used the absorption of the AlF molecule for the determination of F in toothpaste in a nitrous oxide-acetylene flame. Aramendia et al.[35] finally used the absorption of the AlF molecule for the determination of Al in whole blood samples. Ozbek and Akman[36] also investigated the absorption of the SrF molecule at 651.187 nm without a modifier for the determination of F in water samples; however a relatively high detection limit of 36 μg L^{-1} F was obtained.

More recently the absorption of the CaF molecule at the band head at 606.440 nm was proposed for the determination of F in tea (infusion, and after acid digestion or alkaline solubilization)[37] and later also used for the analysis of milk.[38] One of the advantages of this approach is that calcium acts both as the molecule-forming reagent and as a chemical modifier, so that no other reagent had to be added. Another advantage is that the molecular absorption band is in the visible range of the spectrum, where only very few atoms have absorption lines, so that the risk for spectral interferences is minimum. Generally, continuous background absorption is corrected automatically using correction pixels and any direct line overlap can be avoided using a different line of the rotational spectrum. In the case of an overlap with another molecular spectrum, the so-called least squares background correction can be used to correct for this potential interference.[24] Thirdly, although this might not be an obvious advantage, the sensitivity of the CaF molecular absorption is about an order of magnitude lower than that of the GaF; however, in practical analysis this reduces significantly the problem of high blank values, which are often a problem with the

latter molecule. Fluorine is a frequent contaminant in many reagents, and it might also leach out of PTFE vessels in an uncontrolled way during microwave-assisted digestions.

The goal of the present work was to further investigate the applicability of the determination of F via the molecular absorption of CaF at 606.440 nm using direct solid sample analysis of plant material. The motivations for this investigation have been: firstly, to improve the limits of detection, as the samples are introduced into the GF without any dilution; secondly, to increase the sample throughput, as essentially no sample preparation is involved in the analysis (except for grinding, which, however, is also necessary for acid digestion); and thirdly, to further reduce the risk of contamination, as it was for example observed that fluorine is leaching out of the PTFE vessels during a microwave-assisted acid digestion.

2. Experimental

2.1. Instrumentation

A high-resolution continuum source atomic absorption spectrometer Model contrAA 700 (Analytik Jena) was employed for the determination of fluorine throughout this work. This instrument is equipped with a flame and a graphite furnace atomizer in two separate sample compartments, and a xenon short-arc lamp with a nominal power of 300 W, operating in a hot-spot mode, which emits a spectral continuum between 190 and 900 nm. The high-resolution double monochromator with a linear charge coupled device (CCD) array detector with 588 pixels has a spectral resolution of about 1.5 pm per pixel at 200 nm and about 4.5 pm per pixel at 600 nm. The molecular absorption was measured using center pixel (CP) at 606.440 nm and the two adjacent pixels at each side (CP±1).

Transversely heated and pyrolytically coated solid sampling (SS) graphite tubes (Analytik Jena, Part No. 407-A81.303) and SS graphite platforms (Analytik Jena, Part No. 407-152.023) were used for all measurements. An M2P microbalance (Sartorius, Göttingen, Germany) was used for

weighing the samples directly onto the SS platforms. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessory (Analytik Jena), was used to transfer the SS platforms to the atomizer. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas with a flow rate of 2.0 L min^{-1} during all stages, except during vaporization, where the internal flow was stopped. The optimized graphite furnace temperature program used for all the determinations is shown in Table 1.

2.2 Reagents

Distilled, deionized water with a specific resistivity of 18.2 MΩ cm, from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used for the preparation of the standard solutions. The nitric acid (Merck, Darmstadt, Germany) was further purified by sub-boiling distillation in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany). All containers and glassware were soaked in 1.4 mol L^{-1} nitric acid for at least 24 h and rinsed three times with deionized water before use. Sodium fluoride, NaF (Merck) was used to prepare the fluoride standard solutions and calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (Vetec, Duque de Caxias, Brazil) was used as the source of calcium and blank solution.

2.3 Sample Preparation and Procedure

Two certificate materials were used for method validation: NCS ZC73014 - Trace Elements in Tea - and NCS DC73349 - Trace Elements in Bush branches and leaves (China National Analysis Center for Iron and Steel, Beijing, China). Five commercially available plant samples, acquired in different parts of the world, including Europe and Latin America, have been used in this work.

The sample pre-treatment consisted of grinding the samples in a ball mill (Fritsch, Idar-Oberstein, Germany) for 10 min. The particle size was controlled using a 250-μm polyester sieve so

that all particles passed through the sieve. The sample mass, weighed directly onto the SS platform and introduced into the graphite furnace for SS-GF MAS, was typically around 0.1 mg. Ten µL of a solution containing 1500 mg L^{-1} Ca (15 µg Ca) was injected direct onto the sample. For the aqueous standards a volume of 10 µL was injected onto the platform and 10 µL of the molecule-forming reagent added.

3. Results and discussion

3.1 Method development

3.1.1 Optimization of the amount of calcium

Once the target molecule has been selected, it is necessary to optimize the mass of molecule-forming reagent required to quantitatively convert the analyte into this compound. An aqueous standard solution containing 3 ng F as sodium fluoride was injected into the graphite furnace, and the mass of calcium added as the nitrate varied between 0 and 50 µg. The integrated absorbance signal of the CaF molecule increased rapidly up to a mass of 10 µg Ca, as shows the Figure 1, and remained almost constant for higher Ca concentrations. A mass of 15 µg Ca has been used as the molecule-forming element for all future experiments.

3.1.2 Pyrolysis and vaporization curves

The pyrolysis curves for an aqueous standard solution of 3 ng F and the CRM NCS ZC73014, Trace Elements in Tea, normalized for a sample mass of 0.05 mg, are given in Figure 2. The integrated absorbance increased significantly when the pyrolysis temperature was increased from 600 ºC to 800 ºC, particularly for the aqueous standard solution. Kind of a plateau was obtained between 800 ºC and 900 ºC, and the sensitivity decreased only slightly for higher pyrolysis temperatures. This is a very unusual behavior when compared to a typical pyrolysis curve in AAS, where an increase in temperature usually has very little influence on the integrated absorbance

signal at low pyrolysis temperatures, whereas the sensitivity drops rapidly due to losses of the analyte when the maximum (optimum) pyrolysis temperature is exceeded. The increase of the integrated absorbance for the aqueous standard solution by a factor of seven for an increase of the pyrolysis temperature from 600 ºC to 800 ºC indicates that the pyrolysis temperature apparently plays an important role in the process of molecule formation, as will be discussed in more detail in Section 3.5. A pyrolysis temperature of 900 ºC has been chosen for all further investigations. This temperature is higher than those reported in literature [23,36,37], and it is particularly interesting that even a pyrolysis temperature of 1100 ºC could have been used without significant loss of sensitivity, whereas in previous work of our group [36] the analyte was completely lost at this pyrolysis temperature; this will also be discussed in more detail in Section 3.5.

The vaporization curves for the CaF molecule in an aqueous standard solution of 3 ng F and the CRM NCS ZC73014, Trace Elements in Tea, normalized for a sample mass of 0.05 mg, are shown in Figure 3. These curves exhibited a normal pattern with a maximum at 2000 ºC for both the aqueous standard and the CRM, and this vaporization temperature has been chosen for all future experiments. It is worth mentioning that this vaporization temperature is lower than that reported in previous studies that used CaF for the determination of fluorine.[37,38]

3.1.3 Influence of sample mass

In order to investigate if the sample mass introduced into the graphite tube has an influence on the determination, different masses of the CRM NCS ZC73014 were investigated. The correlation between the integrated absorbance signal and the sample mass was linear in the mass range from 0.045 to 0.125 mg; a deviation from linearity has been observed for greater sample masses. Sample masses around 0.1 mg were typically used in this work, and the integrated absorbance was normalized to 0.05 mg or 0.1 mg for better comparison of the results.

3.2 Method validation

3.2.1 Figures of merit

The figures of merit of the developed method are summarized in Table 2. The limit of detection (LOD) is defined as three times the standard deviation of 10 measurements of the blank solution, divided by the sensitivity (slope of the calibration curve), and the limit of quantification (LOQ) as ten times the standard deviation, based on the same measurements. The characteristic mass (m_0) is defined as the mass of analyte corresponding to an integrated absorbance of 0.0044 s. Calibration curves have been established with a blank and six calibration solutions in the concentration range 0.05–10 mg L^{-1} F (0.5–10.0 ng F). The characteristic mass and LOD, pipetting 10 µL solution, were around three and seven times, respectively, lower than those found by Ozbek and Akman (44 pg and 0.26 ng F)[38] and around 50 times lower than those found by Morés et al. (2.5 ng and 1.6 ng F).[37] Potential reasons for this will be further discussed in Section 3.5.

3.2.2 Accuracy, precision and analytical results

The result obtained for F in two CRM using calibration with aqueous standards is shown in Table 3. No significant difference was observed between the certified and the found values for both materials, based on a Student t-test at a 95% confidence level. In order to test the precision of the method, expressed as relative standard deviation (RSD), 10 replicates of the same sample were analyzed and the RSD was around 8%. The average and standard deviations (sd) of five measurements of the five real samples are also shown in Table 3.

Figure 4 shows the time-resolved molecular absorbance spectrum for the laurel leaves. The concentration of fluorine in the CRM and all samples could be determined without any spectral interference.

3.2.3 Comparison of the results

Table 4 shows a comparison of the conditions used and the sensitivity (as m_0) and LOD obtained in the papers published up to now using HR-CS GF MAS for the determination of fluorine. It is obvious that GaF provides the best sensitivity and LOD; however, sensitivity is not always the key issue, and it might become a burden when contamination due to regents and/or digestion vessels becomes significant. An additional concern is the relatively low maximum pyrolysis temperature, which might be no problem for water samples or other samples with a "light" matrix, such as completely digested and/or strongly diluted ones. In this case, however, the advantage of the high sensitivity is at least in part lost due the high dilution during sample preparation.

AlF has a relatively broad absorption band, the fine structure of which is not well resolved, so that background correction might become problematic. The LOD using the SrF absorption band is not really favorable, but it might be an alternative for the determination of high fluorine concentrations.

The absorption of the CaF molecule, which has been used in this work, appears to be an interesting object to consider in more detail the reactions that are going on in the molecule-formation process, and the big difference in sensitivity and thermal stability found even in our laboratory (this work and Ref.[37]) clearly need an explanation. Firstly, exactly the same kind of equipment and graphite furnace that has been used in this work was also used by Morés et al.[37] and Ozbek and Akman.[38] The only major difference is that in the present work solid samples have been analyzed directly, and the corresponding SS graphite tube without a dosing hole and a SS platform have been used also for the analysis of aqueous standard solutions. This might seem a minor difference, however, the SS platform has a significantly greater mass than the PIN platform used for the analysis of liquid and dissolved/digested samples. This greater mass inevitably causes a slower heating rate and maybe even a lower final temperature, which could explain the higher pyrolysis

temperature of 900 ºC found in this work. However, it cannot explain, why only a slightly lower sensitivity has been obtained even at a pyrolysis temperature of 1100 ºC, a temperature where in earlier work[37] no signal at all could be recorded any more. It can also not explain why the maximum sensitivity has been obtained already at a vaporization temperature of 2000 ºC instead of 2250 ºC, as in earlier work.[37,38] This means that there might be other reactions going on in the pyrolysis stage, which are not yet well understood and will need more research in the future.

One possible explanation might be that fluorine in plants is at least in part organically bound and lost in an unknown form at low pyrolysis temperatures. With increasing pyrolysis temperature this fluorine is more efficiently bound to Ca, most likely as CaF_2, which has a melting point of 1418 ºC, which also explains the high thermal stability of the fluorine compound. In the case of digested samples, the presence of nitric acid or its decomposition products, which have been shown to intercalate into the graphite structure and remain up to very high temperatures,[39] might cause completely different reactions and hence volatilities of the respective fluorine compounds.

The other difference is the SS graphite tube without a dosing hole. Güell and Holcombe[40-42] published several papers where they tried to calculate the influence of the dosing hole (among other parameters) on the analyte loss during the atomization process in AAS. Silva et al.[43] also found an about 4-5 times better sensitivity for mercury in an SS graphite tube without dosing hole compared to published values using regular tubes. In MAS the effect of the dosing hole (or its absence) might be even more pronounced, as in the absence of a dosing hole not only the loss of analyte through this orifice is avoided, but the longer residence time of the analyte and the molecule-forming reagent in the graphite tube might as well increase the reaction between the species and result in a more efficient formation of the target molecule, and hence result in an even higher sensitivity.

Obviously, all the above considerations might be termed as speculation; however, this speculation might stimulate new research that finally will shed more light on this new field of research that we have just started to enter.

4. Conclusion

A method has been developed for the determination of total fluorine in plant material using the molecular absorption of the CaF molecule in a graphite furnace, direct solid sample analysis and calibration against aqueous standard solutions. The pyrolysis temperature that could be used in this work has been significantly higher and the vaporization temperature lower than in previously published papers using this technique. The sensitivity and limit of detection obtained in this work is also significantly better than values that were reported in the literature, including those produced in our own laboratory. An attempt to explain some phenomena, however it was taken, it is clear that much more research is needed using MAS. Evidently, is necessary to fully clarify the reasons for the differences in sensitivities and gain better control of HR-CS GF MAS. The authors hope that this manuscript could stimulate other researchers to dig into this matter and contribute to finding solutions and explanations.

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Figure captions

Figure 1. Effect of the mass of Ca on the CaF molecular absorption of 3 ng F.

Figure 2. Pyrolysis curves for (■) 3 ng fluorine in an aqueous standard solution; (●) fluorine in CRM NCS ZC73014, normalized for 0.05 mg of sample. T_{vap} = 2000 °C.

Figure 3. Vaporization curves for (■) 3 ng fluorine in an aqueous standard solution; (●) fluorine in CRM NCS ZC73014, normalized for 0.05 mg of sample. T_{pyr} = 900 °C.

Figure 4. Time-resolved absorbance spectrum for the CaF molecule in the vicinity of the 606.440 nm analytical line recorded for the laurel leaves. T_{pyr}= 900 °C; T_{at}= 2000 °C.

Table 1. Temperature program used for the determination of fluorine via the molecular absorption of CaF using HR-CS GF MAS.

Stage	Temperature / °C	Ramp / °C s^{-1}	Hold time / s
Drying	90	5	20
Drying	140	5	10
Pyrolysis	900	500	30
Vaporization	2000	3000	4
Cleaning	2200	1000	4

Table 2. Figures of merit for the determination of fluorine via CaF using HR-CS GF MAS in the presence of 15 µg Ca as the molecule-forming reagent.

Linear regression equation	r	LOD*/ ng	LOQ*/ ng	LOD** / µg g^{-1}	LOQ** / µg g^{-1}	m_0 / pg
A_{int} = 0.0056 + 0.0975 ng_F	0.9990	0.036	0.12	0.36	1.20	44

*absolute / **relative (0.1 mg of sample)

Table 3. Fluorine determination in CRM and plant materials using HR-CS GF MAS in the presence of 15 µg Ca as the molecule-forming reagent (n=5).

CRM and samples	Certified µg g^{-1}F ± uncertainty	Found µg g^{-1} F ± standard deviation
NCS DC 73349	23 ± 4	22 ± 2
NCS ZC 73014	57 ± 15	62 ± 5
Laurel	-	4.9 ± 0.4
Parsley	-	3.5 ± 0.3
Dried seaweed	-	2.7 ± 0.2
Horseradish	-	3.4 ± 0.3
Virginia Tobacco CTA-VTL-2	-	29 ± 2.1

Table 4. Comparison of the conditions used and the figures of merit reported in the literature about the determination of fluorine using HR-CS GF MAS.

Author	Target molecule	T_{pyr} / ºC	T_{vap} / ºC	m_0 / pg	LOD / pg
This work	CaF	900	2000	44	36
Morés et al.[37]	CaF	725	2250	2500	1600
Ozbek and Akman[38]	CaF	700	2250	130	260
Heitmann et al.[28]	GaF	500	1400	13	9
Gleisner et al.[29]	GaF	550	1550	7.4	5.2
Gleisner et al.[30]	GaF	550	1550	7.4	5.2
Krüger et al.[31]	GaF	700	1600	n.a.*	230
Bücker and Acker[33]	AlF	600	2100	13	145
Ozbek and Akman[36]	SrF	800	2200	550	360

*n.a = not applicable

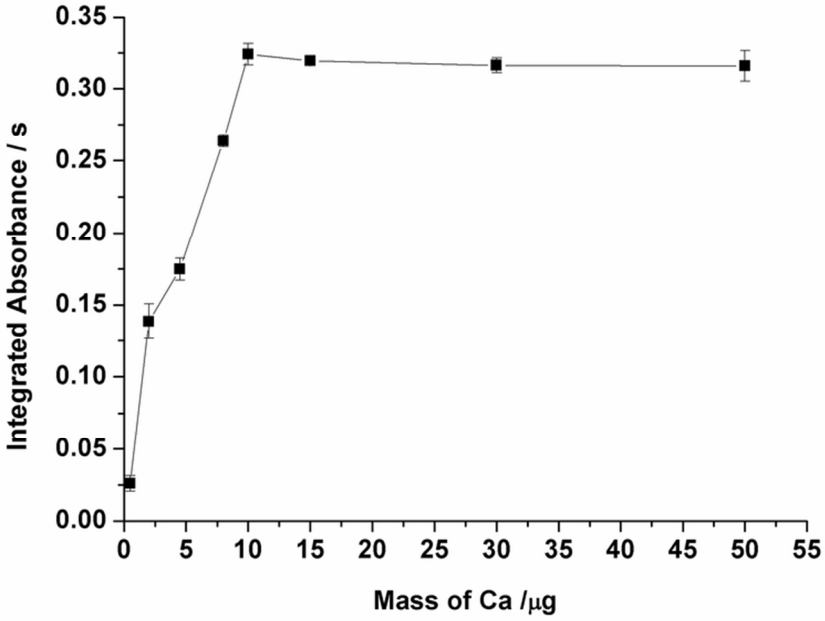


Figure 1. Effect of the mass of Ca on the CaF molecular absorption of 3 ng F.
76x53mm (300 x 300 DPI)

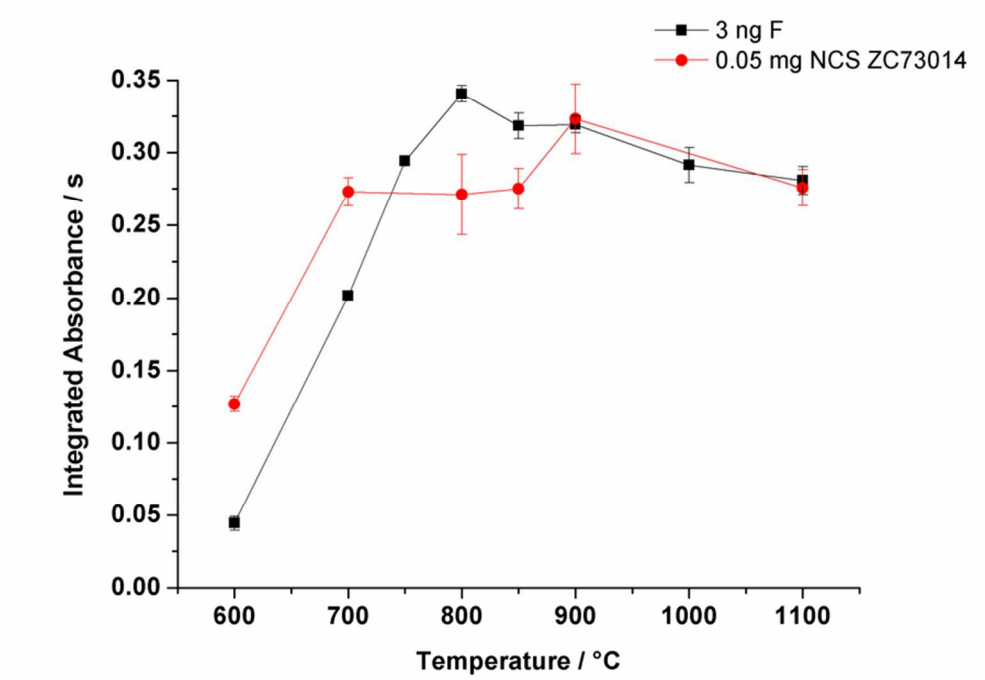


Figure 2. Pyrolysis curves for (■) 3 ng F in an aqueous standard solution; (□) fluorine in CRM NCS ZC73014, normalized for 0.05 mg of sample. Tvap = 2000 °C.
77x54mm (300 x 300 DPI)

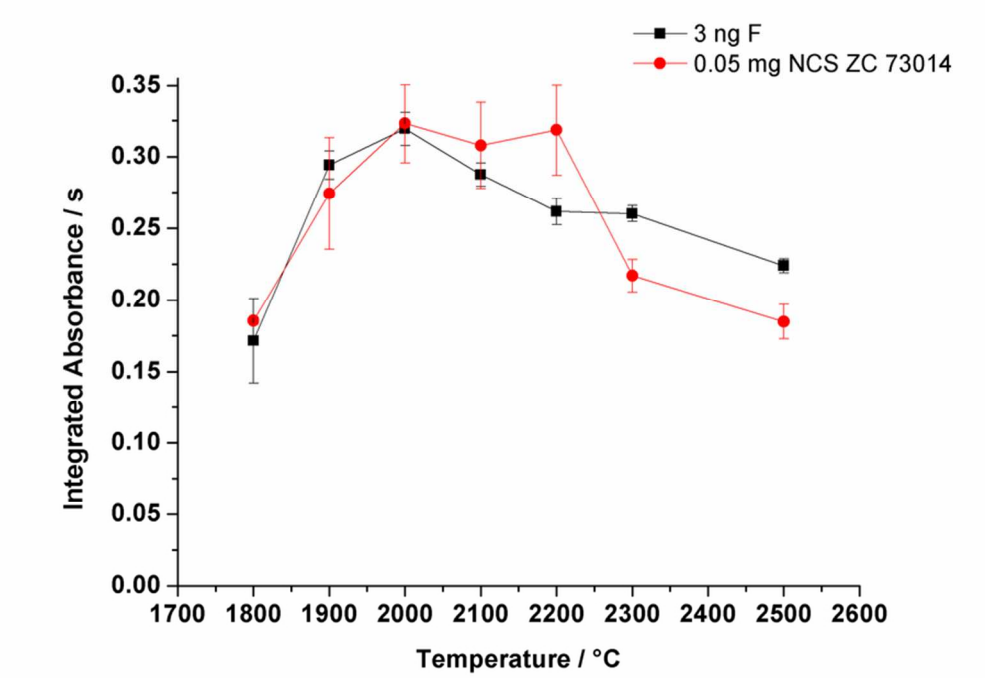
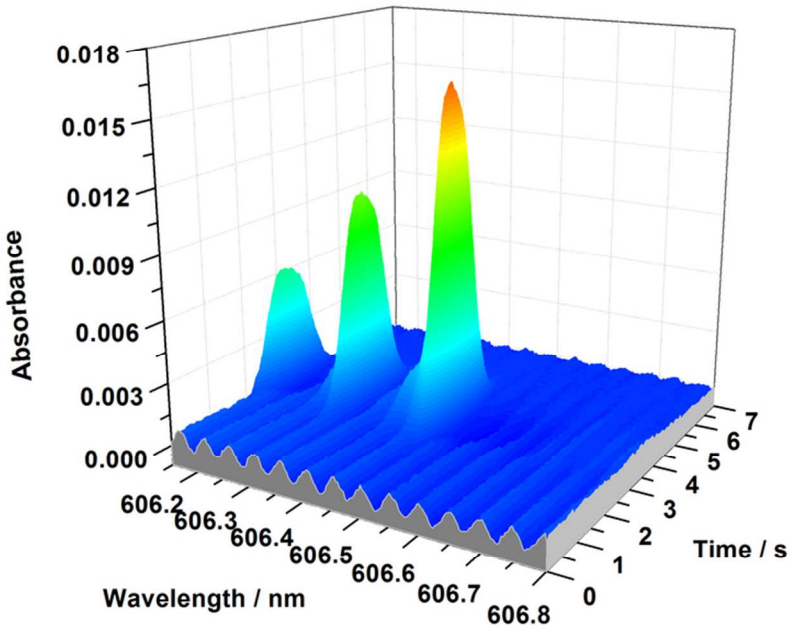
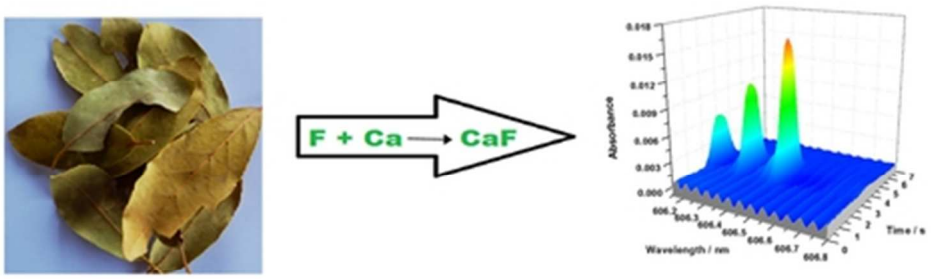


Figure 3. Vaporization curves for (■) 3 ng F in an aqueous standard solution; (□) fluorine in CRM NCS ZC73014, normalized for 0.05 mg of sample. Tpyr = 900 °C.
77x54mm (300 x 300 DPI)



77x54mm (300 x 300 DPI)



Fluorine reacts with calcium forming gaseous CaF, which can be determined by high-resolution molecular absorption spectrometry.
39x19mm (300 x 300 DPI)