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Determination of fluorine in tea using high-resolution molecular absorption spectrometry with electrothermal vaporization of the calcium mono-fluoride CaF

Silvane Morés [a], Gustavo C. Monteiro [a], Flaviane da Silva Santos [a], Eduardo Carasek [a], Bernhard Welz [a,b,*]

[a] Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis – SC, Brazil
[b] Instituto Nacional de Ciência e Tecnologia – INCT de Energia e Ambiente, UFBA, Salvador – BA, Brazil

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ABSTRACT

High-resolution continuum source molecular absorption of the calcium mono-fluoride molecule CaF in a graphite furnace has been used to determine fluorine in tea after acid digestion, alkaline solubilization and preparation of a conventional aqueous infusion. The strongest absorption 'line' of the CaF molecule is at 606.440 nm, which is part of the rotational fine structure of the $X\,^2\Sigma^+ - A\,^2\Pi$ electronic transition; it has a bond dissociation energy of 529 kJ mol^{-1}, which is comparable with other molecules used for fluorine determination. One advantage of using Ca as the molecule-forming reagent is that spectral interferences are extremely unlikely in the spectral range of its strongest absorption. Another advantage is that Ca acts both as molecule forming reagent and chemical modifier, so that no other reagent has to be added, making the method very simple. The only disadvantage is that Ca has a somewhat negative influence on the graphite tube lifetime. The limit of detection was found to be 0.16 mg L^{-1} F, corresponding to 1.6 ng F absolute, and the calibration curve was linear in the range between 0.5 and 25 mg L^{-1} with a correlation coefficient of $R = 0.9994$. The results obtained for a certified tea reference material were in agreement with the certified value on a 95% confidence level. There was also no difference between the results obtained after an acid digestion and an alkaline solubilization for 10 tea samples, based on a paired *t*-test. The values found in the 10 samples ranged between 42 μg g^{-1} and 87 μg g^{-1} F; the tea infusions contained between 21 μg g^{-1} and 56 μg g^{-1} F, with an extraction rate between 48% and 74%.

1. Introduction

Fluorine and several of its compounds are extremely toxic, but the fluoride ion 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. For these reasons fluoride has to be determined routinely in a variety of samples [1–4].

Tea is one of the most important non-alcoholic beverages, and about two third of the world's population consume it daily in the morning [5], and many of them also throughout the day. The plants used to make tea are well known to accumulate fluoride [6–8], and the fluorine content might even be used as a parameter for judging the tea quality [9]. Moderate consumption of tea has several health benefits, and one of them is the attenuation of dental caries due to the presence of fluoride [10]. Excessive consumption of tea with high levels of fluoride, however, increases the risk of dental fluorosis, particularly in countries where the water is already enriched with this element [11,12]. The occurrence of this disease has already been documented in countries like China, where tea is a very popular beverage, and often consumed all day long [13,14].

The determination of fluoride is widely described in the literature and is well-reviewed for example by Huang et al. [15]. The methods range from classical gravimetric and volumetric methods over photometric [1] and electrochemical methods, such as fluoride ion selective electrode (ISE) [4], to ion chromatography (IC) [16–18]. Predominating methods nowadays are ISE and IC; the ISE is easy to use, cost-effective and suitable for continuous monitoring, whereas IC is more expensive and requires better trained personnel. Common for both methods is the response for only free fluoride ions; organic or covalently bonded F cannot be detected, making the application practicable only for aqueous systems. Ions such as Al^{3+}, Si^{4+}, Mn^{3+}, Mn^{2+}, and Fe^{3+} or water-soluble organic compounds form complexes with, and/or absorb free fluoride ions, causing serious interferences resulting in low recoveries.

Fluorine is the most electronegative element with a very high ionization potential of 17.42 eV, and its resonance lines are located in the vacuum-UV range below 100 nm. Hence, the use of

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* Corresponding author at: Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis – SC, Brazil. Tel.: +55 48 3733 8876; fax: +55 48 3721 6850.
E-mail address: welz@qmc.ufsc.br (B. Welz).

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spectrometric methods such as inductively coupled plasma optical emission spectrometry (ICP OES) or atomic absorption spectrometry (AAS) is not feasible for fluorine determination. Similarly, inductively coupled plasma mass spectrometry (ICP-MS) is also not capable to determine fluorine, as the ionization potential of the argon plasma is not sufficient to ionize this element, unless electrothermal vaporization is used for 'dry' sample introduction [19,20].

Molecular absorption spectrometry (MAS) in flames and furnaces was proposed as an alternative for fluorine determination already in the 1970s, as summarized in recent Review articles [21,22]. Particularly Dittrich [23,24] and Tsunoda et al. [25] investigated molecular absorption spectra of gallium, indium and aluminum mono-halides in graphite tube furnaces, and aluminum mono-fluoride was applied in most of the later applications for quantitative fluorine determination using MAS. Dittrich [23,24] used a dual-channel spectrometer and a hydrogen hollow cathode lamp (HCL) for his investigations; in all the other studies conventional line source AAS was used with a platinum HCL, as one of the lines emitted by the latter coincided accidentally with the AlF spectrum, and D_2 background correction. Electron excitation spectra of diatomic molecules such as AlF, which are found in the UV and visible range of the spectrum, are characterized by a pronounced rotational fine structure [21,22,26]. The spectrometers normally used for classical AAS are not capable of resolving this fine structure, resulting in spectral interferences and background correction errors when applied for MAS, so that this approach never found general acceptance.

In the last decade, however, the development and commercial availability of equipment for high-resolution continuum source AAS (HR-CS AAS) [26] has shed new light on the determination of non-metals using MAS [21,22], and the determination of fluorine using HR-CS MAS was described by Huang et al. [15] for flame MAS, and by Heitmann et al. [27] using a graphite furnace. The main advantage using this new technique is indeed the high resolution provided by the double monochromator with a prism for pre-dispersion and an echelle grating for highest resolution [26] that almost completely resolves the fine structure of the molecular bands, avoiding at the same time spectral interference and background correction errors [21,22]. In both of the above papers the GaF molecular absorption band head at 211.248 nm was chosen instead of the AlF spectrum because of its narrower profile and greater freedom from spectral interference [15,27]. Gleisner et al. [28] optimized the procedure, making it more robust using various additives and modifiers; however, at the expense of a more complex procedure, and a relatively high blank value due to the large quantities of reagents that had to be added. Later, Gleisner et al. [29] applied the procedure for the determination of fluorine in toothpaste.

The goal of this work has been to develop a simple and reliable method for the determination of fluorine in tea using MAS and a commercially available high-resolution continuum source atomic absorption spectrometer with electrothermal vaporization for the generation of the target molecule. At the same time we were trying to simplify the method described by Gleisner et al. [28], searching for other molecule-forming agents and avoiding the large number of reagents that were necessary for this procedure, as the proposed method was intended for routine application.

2. Experimental part

2.1. Instrumentation

A high-resolution continuum source atomic absorption spectrometer Model contrAA 700 (Analytik Jena AG, Jena, Germany) with a flame and a transversely heated graphite tube atomizer in two separate sample compartments was used for all measurements. The instrument is equipped with a 300 W xenon short-arc lamp, operating in a hot-spot mode, as continuous radiation source for the wavelength range from 185 to 900 nm, a high-resolution double monochromator, consisting of a prism pre-monochromator and an echelle grating monochromator, providing a spectral bandwidth per pixel of about 2 pm at 200 nm, and a linear charge coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytical purposes, displaying the vicinity of the analytical line at high resolution.

All measurements were performed using the graphite furnace technique and pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025) and a sample volume of 10 μL. The integrated absorbance of three pixels has been added (peak volume selected absorbance, PVSA, $A_{\Sigma 3,\mathrm{int}}$) [30], resulting in the best signal-to-noise ratio. The temperature program used for vaporization and determination of fluorine via the CaF molecular absorption at 606.440 nm is shown in Table 1.

Table 1
Temperature program used for the determination of fluorine via the molecular absorption of CaF using HR-CS ET MAS; argon purge gas flow rate 2.0 L min^{-1} in all stages except during vaporization, where the gas flow was interrupted.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)
Drying 1	80	6	10
Drying 2	110	5	10
Pyrolysis	725	300	10
Vaporization	2250	3000	5
Cleaning	2650	500	4

2.2. Reagents, samples and sample pre-treatment

Distilled and deionized water obtained from a Model Mega ROUP Megapurity system (Equisul, Pelotas, Brazil) was used throughout for sample dilution and preparation of calibration solutions. Potassium fluoride, KF (Merck, Darmstadt, Germany) 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. Nitric acid, HNO_3 (Aldrich, St. Louis, MA, USA) was further purified by subboiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). Tetramethyl ammonium hydroxide, TMAH, 25% (Merck) was used for alkaline solubilization of the samples.

One Tea Reference Material, NCS–ZC73014 (China National Analysis Center for Iron and Steel – Beijing, China) with a certified content of 57 ± 15 μg g^{-1} F was used for method validation, and 10 commercially available tea samples, acquired in different parts of the world, including China, Europe and Latin America, have been used in this work.

The samples have been prepared in three different ways: firstly, using microwave-assisted acid digestion using a TOPwave laboratory microwave oven (Analytik Jena) with contact-free temperature and pressure control in each of the eight digestion vessels. Approximately 500 mg of the tea samples were weighed accurately into the PTFE vessels of the microwave oven, 7.0 mL of concentrated nitric acid was added, the vessels were closed and the program shown in Table 2 was executed. The vessels were allowed to cool down for 30 min, carefully opened and the content diluted to 10 mL with water in a volumetric flask. Secondly, the tea samples were solubilized in TMAH; about 500 mg of sample were weighed accurately into a Teflon vessel, 1.5 mL of 25% TMAH were added and the mixture was kept in a water bath at 75 °C for 40 min. After that the vessels were allowed to cool down for about 1 h and the content was diluted to 10 mL with water in a volumetric flask. Thirdly, infusions of the tea samples were prepared to simulate as close as

Table 2
Temperature and pressure program for the microwave-assisted digestion of about 500 mg of tea in 7 mL HNO_3; the two program steps were executed sequentially, followed by a cooling stage.

Step	01	02
Temperature (°C)	150	190
Pressure (bar)	50	50
Power (%)	70	90
Ramp (min)	5	5
Time (min)	10	20

possible the preparation of tea for daily use. One gram of tea was left in water at 90 °C for 5 min, the extract diluted to 10 mL and analyzed afterwards.

All sample preparations were carried out in triplicate, and each of the solutions was measured at least three times, so that all results are the average of at least 9 measurements. Calibration was carried out against a calibration curve established with aqueous standard solutions, with the same amount of calcium added as to the sample solutions.

3. Results and discussion

3.1. *Measuring fluorine using the molecular absorption of CaF*

In most of the more recent applications of HR-CS MAS for the determination of fluorine with electrothermal vaporization (ETV), gallium fluoride (GaF) was preferred as the target molecule over AlF because of the narrower profile of the GaF band head at 211.248 nm, and its relative freedom from spectral interference. Nevertheless, besides the addition of the molecule-forming reagent gallium, Heitmann et al. [27] had to coat the graphite tube with Zr as a permanent modifier and to add Mg as a modifier in solution in order to get satisfactory results. However, the method was not yet optimized, as the authors found it necessary to use the analyte addition technique to correct for matrix effects. Gleisner et al. [28] further optimized this method using additional modifiers, which resulted in increased sensitivity and robustness, however, at the expense of a more complex procedure, which required a change in the software, and increased blank values.

One of the potential sources of error in MAS is the formation of a ‘competitive molecule’ other than the target molecule of the analyte, which inevitably reduces the concentration of the target molecule in the gas phase, and hence the sensitivity. Calcium is a very common matrix element in water and in many biological and other materials, and the molecular bond dissociation energy of the CaF molecule of 529 kJ mol^{-1} [31], is very close to that of the GaF molecule (577 kJ mol^{-1}), and hence a potential interferent. We therefore decided to investigate the possibility to use the CaF molecular absorption for analytical purposes; the most intense band head is found at 606.440 nm, which is part of the $X\,^2\Sigma^+ - A\,^2\Pi$ electronic transition; the spectrum of the vicinity of this band head is shown in Fig. 1. Another advantage of this line is that it is located in the visible range of the spectrum, where the risk of spectral interference is much lower than in the low UV-range.

3.2. *Molecule-forming reagent and modifiers*

First of all the amount of calcium had to be defined in order to obtain the maximum concentration of CaF in the gas phase during ETV of the molecule. In a first experiment, 20 μL of an aqueous standard of 15 mg L^{-1} F was used and the molar ratio between calcium and fluoride ([Ca]:[F]) was increased from 0.5 to 27.5, injecting 20 μL of an appropriate calcium standard on top of the fluoride standard in the graphite tube. As is shown in Fig. 2, the sensitivity for the CaF molecular absorption increased almost linearly up to a molar ratio [Ca]:[F] ≈ 20, above which the integrated absorbance value remained essentially constant. In a second experiment the calcium concentration was fixed at 630 mg L^{-1} Ca, and the fluoride concentration varied between 1 mg L^{-1} and 30 mg L^{-1} F; a perfectly linear relationship with a correlation coefficient of $R = 0.9994$ has been obtained, demonstrating that an excess of calcium over the molar ratio [Ca]:[F] = 20 does not have any negative influence on the determination of low fluoride concentrations. The concentration of the molecule-forming reagent was fixed at 630 mg L^{-1} Ca for all future experiments. It is worth mentioning that no platform coating with a permanent modifier or any other chemical modifier has been used in these and all future experiments.

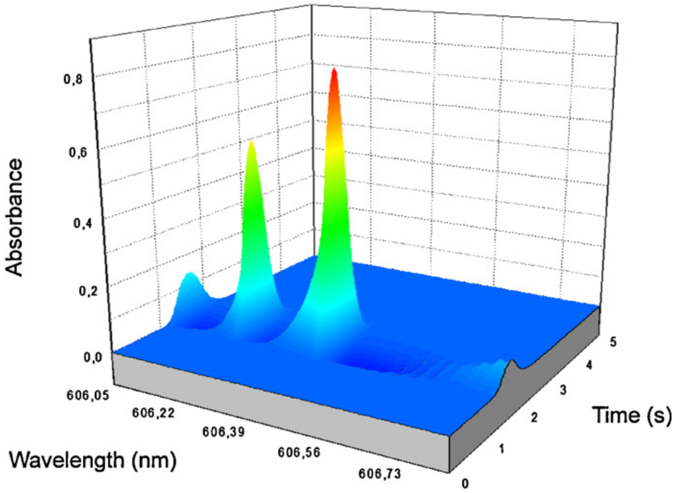

Fig. 1. Time- and wavelength-resolved absorption spectrum in the vicinity of the CaF band head at 606.440 nm.

3.3. *Pyrolysis and vaporization curves*

Similar to electrothermal atomization, pyrolysis and vaporization (instead of atomization) curves have to be established for MAS in order to avoid analyte losses and to find the conditions for best sensitivity. Pyrolysis and vaporization curves for the CaF molecule are shown in Fig. 3a and b, respectively. The pyrolysis curve exhibits a very pronounced maximum at 725 °C and significantly lower sensitivity for lower pyrolysis temperatures. This might be

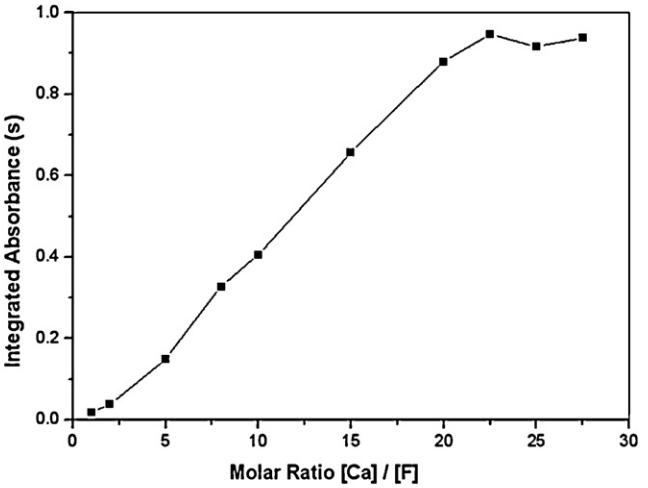

Fig. 2. Correlation between the integrated absorbance measured for the CaF molecular absorption of a 15 mg L^{-1} F standard solution and the molar ratio ([Ca]:[F]) of an added calcium standard solution.

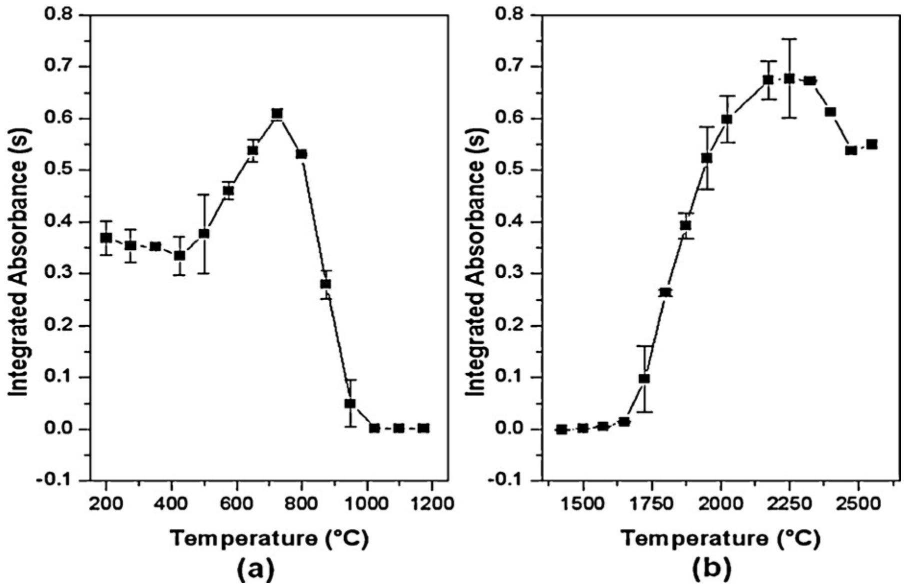

Fig. 3. Optimization of the conditions for the electrothermal vaporization and determination of F via CaF molecular absorption using 20 μL of a 15 mg L^{-1} F standard solution; (a) pyrolysis curve using a vaporization temperature of 2250 °C; (b) vaporization curve using a pyrolysis temperature of 725 °C.

an indication that around this temperature some reaction is going on that favors the later formation of the gaseous CaF molecule. The sharp drop of the pyrolysis curve above 800 °C and the fact that no signal at all can be measured between about 900 °C and 1700 °C is an indication that fluorine is lost in some form, other than CaF in this temperature range. This means that the temperature interval between the optimum pyrolysis temperature and the vaporization temperature of 2250 °C has to be covered with a high heating rate in order to avoid analyte losses. The pyrolysis and atomization curves for the samples after digestion were very similar to those for the aqueous solution and are not shown here. Actually, the maximum at 725 °C in the pyrolysis curve was even more pronounced for the sample solution, and the vaporization curve also exhibited a clear maximum between 2200 °C and 2250 °C. Both, the pyrolysis and the vaporization temperatures found in this work are significantly higher than the values published by Heitmann et al. [27] of 500 °C and 1400 °C and Gleisner et al. [28,29] of 550 °C and 1550 °C, respectively, for the GaF molecule.

3.4. Figures of merit and validation

The figures of merit of the developed method are summarized in Table 3, both in concentration and in absolute values, based on 20 μL of injection volume. The limit of detection (LOD) is defined as three times the standard deviation of a 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. Calibration was performed against a calibration curve established with 10 aqueous standard solutions in the concentration range 0.5–25.0 mg L^{-1} F. The resulting linear regression equation was:

$$A_{\text{int}} = 0.0037 + 0.0179c_{\text{F}}$$

Ten blank measurements for the aqueous solution gave an average and standard deviation of $A_{\text{int}} = 0.0046 \pm 0.0009$, whereas the values for the acid digestion and the alkaline solubilization were $A_{\text{int}} = 0.0045 \pm 0.0011$, and $A_{\text{int}} = 0.0043 \pm 0.0001$, respectively. These values clearly demonstrate that there was no detectable amount of fluorine leaching from the PTFE vessels during the digestion or solubilization processes.

For validation purposes a Tea Reference Material (NCS-ZC73014) with a certified value of 57 ± 15 μg g^{-1} F was subject to a microwave-assisted acid digestion and also solubilized using TMAH (refer to Section 2). The result obtained with the former sample pretreatment was 51 ± 12 μg g^{-1} F, and with the latter one 56 ± 6 μg g^{-1} F. Both values were not significantly different from the certified vale on a 95% confidence level.

The sensitivity obtained at the CaF molecular absorption band head at 606.440 nm is more than two orders of magnitude lower than that reported by Heitmann et al. [27] and Gleisner et al. [28,29] for the GaF line at 211.248 nm. This, however, was not considered a disadvantage, as the sensitivity obtained at the former line perfectly served the purpose, avoiding the need for excessive dilution. In addition, the relatively high blank value reported by Gleisner et al. [28,29] also was not observed in this work.

Table 3
Figures of merit for the determination of fluorine using HR-CS ET MAS and a calibration curve established with aqueous standard solutions for fluoride in the presence of calcium as the molecule-forming reagent; all measurements were in integrated absorbance using three pixels.

Parameter	Relative	Absolute
Limit of detection (n = 10)	0.16 mg L^{-1}	1.6 ng
Limit of quantification (n = 10)	0.52 mg L^{-1}	5.2 ng
Characteristic concentration	0.25 mg L^{-1}	
Characteristic mass		2.5 ng
Sensitivity (B)	0.0179 s L mg^{-1}	
Correlation coefficient (R)	0.9994	0.9994
Linear working range	0–25 mg L^{-1}	5–250 ng

3.5. Analysis of tea samples

Ten tea samples from different parts of the world have been acquired and brought into solution using both an acid digestion and an alkaline solubilization, and also preparing a conventional tea infusion, as described in Section 2. The results are presented in Table 4, and there is no significant difference between the results obtained with the two digestion/solubilization procedures on a 95% confidence level. The fluorine content in the different tea samples was between 42 μg g^{-1} and 87 μg g^{-1}, but with no detectable tendency for the different brands of tea. According to expectation, the infusions had lower fluoride content with an extraction rate

Table 4
Values obtained for fluorine in tea samples using HR-CS ETV MAS of the CaF molecule at 606.440 nm, using acid digestion, alkaline solubilization and regular infusion.

Sample	Acid digestion ($\mu g\,g^{-1}$)	Alkaline solubilization ($\mu g\,g^{-1}$)	Infusion ($\mu g\,g^{-1}$)	Extraction to infusion (%)
Darjeeling FOP	59 ± 11	60 ± 12	37 ± 8	62
Longjing tea	47 ± 15	44 ± 15	27 ± 10	59
Earl Gray	67 ± 12	67 ± 14	49 ± 15	73
Darjeeling	76 ± 9	79 ± 11	40 ± 13	52
White tea	42 ± 7	45 ± 12	21 ± 11	48
Green tea with passion fruit	63 ± 12	64 ± 10	47 ± 17	74
Green tea with lemon	64 ± 17	67 ± 14	39 ± 13	59
Black tea 1	50 ± 13	49 ± 13	26 ± 13	52
Black tea 2	85 ± 19	87 ± 16	55 ± 17	65
Mate tea	50 ± 11	49 ± 9	29 ± 10	59

between 48% and 74% of the total content. Nevertheless, tea might be a significant source of fluorine in countries with a high consumption of this beverage.

4. Conclusion

A simple procedure has been developed for the determination of fluorine in tea using the molecular absorption of CaF after electrothermal vaporization in a graphite tube furnace. The great advantage is that only calcium has to be added in a 20-fold molar excess over fluorine as the molecule-forming agent, and no other modifier was necessary. The only disadvantage is that the graphite tubes last for only about 100 determinations due to the well-known reaction of calcium with graphite under the formation of a carbide, which decomposes upon the addition of water. The sensitivity of the proposed method is lower than that described for the GaF molecular absorption, but it perfectly served the purpose, and the CaF absorption line at 606.440 nm might well be applicable for the determination of fluorine in other types of samples in case the analyte concentration is high enough.

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