The use of microwave-induced plasma optical emission spectrometry for fluorine determination and its application to tea infusions

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ARTICLE INFO

Keywords: Fluorine CaF MIP-OES Emission spectrometry Tea HR-GF MAS

ABSTRACT

This study presents a novel method for fluorine quantification determination by microwave-induced plasma optical emission spectrometry (MIP-OES). Due to the low temperature of this plasma, atomic emission of fluorine could not be measured, instead CaF molecular emissions were measured by using a calcium solution mixed in the spray chamber with the sample using a T-piece. Several wavelengths were studied to find the best signal to noise ratio for fluorine determination and 530.45 nm was chosen. The limit of detection for the determination of fluorine via CaF using MIP-OES was 1.1 mg L⁻¹. A linear response was observed over two orders of magnitude (R² = 0.998). The developed method was applied to ten tea infusion samples from the UK and Saudi Arabia. The results were not significantly different (paired Student’s t-test, p = 0.97) to the results obtained using the reference method, high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-GF MAS). The total fluorine in the tea infusions varied between 2.7 and 7.8 mg L⁻¹; all of which were above the WHO recommended level of fluoride (0.8–1.5 mg L⁻¹) in drinking water. This method can potentially be used for total fluorine determination and might be useful for fluorine speciation analysis when coupled with HPLC.

1. Introduction

Commercially available microwave-induced plasma optical emission spectrometry (MIP-OES) has been used for the elemental determination of many elements including alkaline and earth alkaline metals, transition metals and some metalloids and non-metals, but not fluorine. This technique uses a nitrogen-based plasma to excite atoms, the corresponding emission of which is measured. The temperature achieved by this plasma, approximately 5000 K, is not high enough to produce a sufficient population of excited fluorine atoms for their detection. Additionally, the primary emission lines of the halogens are in the vacuum-UV region, fluorine is no exception with the resonance line at 95.5 nm and it is therefore impossible to determine these elements with conventional optical instruments due to oxygen interference [1,2]. Therefore, the non-resonance line of fluorine at 685.6 nm was used in the past, especially with a helium plasma, which generates a large population of excited fluorine atoms [3]. However, these plasmas tend to have low power, so it is difficult to measure aqueous samples [4]. An ICP-OES with an argon plasma, which is more robust, has successfully been used for F determination in solid samples at non-resonance lines due to the relatively high temperature of about 8000 K [5].

An alternative for the determination of halogens using optical instruments is the generation of a diatomic molecule with the analyte, by the addition of a forming-reagent. This molecule will absorb/emit radiation at a wavelength on the UV-VIS region of the spectra, avoiding the aforementioned difficulties. High-resolution graphite furnace molecule absorption spectrometry (HR-GF MAS) has been used for fluorine determination as metal monofluorides such as CaF [20] or GaF [6]. A similar approach was utilized for elemental mass spectrometry, where metal fluoride cations were generated in an inductively-coupled argon plasma cannot efficiently ionise fluorine to F⁺ [7,8]. Jamari et al. [8,9] used the BaF⁺ ion for fluorine determination by inductively-coupled plasma triple quadrupole mass spectrometry (ICP-MS/MS). Both techniques are, however, expensive and not readily available in low-income countries. There are currently no publications describing a method for halogen determination using a commercially MIP-OES with a nitrogen
plasma, which is more affordable than ICPs. Here we demonstrate that fluorine can be measured using CaF emissions in aqueous tea infusions using a low-temperature nitrogen plasma with MIP-OES.

The importance of an affordable method for fluorine determination is that fluorine in the form of fluoride is an essential element for human health. Recommended daily intake can protect from dental decay and promotes healthy bones [10]. According to the World Health Organization (WHO), the recommended limit of fluoride in drinking water is between 0.8 and 1.5 mg L$^{-1}$ [11]. However, too high fluoride levels can be toxic to humans and cause illnesses such as fluorosis, common in countries where the population uses fluoride rich ground and surface water as potable water [12]. To measure the levels of fluoride in food and beverage is a way to control the daily fluoride intake of a population and avoid health problems. In this context, tea is a well-known source of fluoride for humans, since the plants normally used to make tea contain relatively high concentrations of fluoride [13]. Tea plants are known to be a hyperaccumulator of fluoride [14]. Moreover, the fluoride concentration in tea depends on the origins of the tea, age of the leaves, quality of the brand and growing conditions. According to Chan et al. [10] the total fluoride concentration in tea leaves differs from 15 to almost 3000 mg kg$^{-1}$ depending on the soil properties, hence the influence of location, and between 8 mg kg$^{-1}$ to 1530 mg kg$^{-1}$ depending on the tea plant variety [10]. Fluoride is traditionally measured by ion chromatography and ion-selective electrodes, which has also been applied to tea [15,16]. However, all fluoride needs to be transformed into fluoride and the matrix need to be destroyed to avoid matrix effects. Additionally, tea has been speculated to transform fluoride into natural organofluorines such as toxic fluorooxacetate and other organofluorines such as per and polyfluorinated alkylated substances (PFAS) or fluorinated pesticides may accumulate [26]. To measure total fluoride, the strong C-F bond must be cleaved through a large energy input such as a hot plasma. Fluorine may form CaF in the nitrogen plasma, which has a dissociation energy of 529 kJ mol$^{-1}$. We investigated whether CaF can be used for the total fluoride determination in tea infusion without any sample preparation with this novel affordable approach using MIP-OES for total fluorine. The analysis was evaluated by comparing the results with the complementary method of high-resolution graphite furnace molecular mass spectrometry (HR-GF MAS).

2. Experimental

2.1. Instrumentation

MIP-OES: For the proposed method, all measurements were taken using a commercially available MP-AES 4200 (Agilent Technologies, Santa Clara, CA, US) with a concentric nebulizer and a cyclonic spray chamber. The instrument is coupled with a nitrogen generator which extracts nitrogen from the air while measuring to nebulize the incoming sample to a fine aerosol, as well as form the plasma. The sample containing fluoride was mixed with a calcium solution 1:1 using a T-piece before nebulization. In the plasma, the CaF is formed and excited, emitting light when it relaxes to a lower energy state. The light beam is navigated using mirrors to the monochromator. The wavelength spectrum was scanned to identify the most sensitive emission line with the highest signal to noise ratio. No automatic background correction was used, however, a blank subtraction was applied to the raw extracted data.

HR GF-MAS: For the accuracy evaluation, the results obtained using the described method were compared with the results achieved using a high-resolution continuum source atomic absorption spectrometer Model contrAA 700 (Analytik Jena, Jena, Germany). The spectrometer is equipped with 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 and uses a charge-coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytical purposes. The double monochromator consists of a prism pre-monochromator and an echelle grating monochromator for high resolution. All measurements were performed at the highly sensitive wavelength for CaF molecule at 606.429 nm, using the sum of the integrated absorbance of three pixels (peak volume selected absorbance, PVSA, A23, int) [17]. Pyrolytically coated graphite tubes with PIN platform (Analytik Jena, Part No. 407-A81.025) and with transversal heating were used in all experiments.

A centrifuge, VWR Megastar 600 (Avantor, New Jersey, United states), equipped with four 50 mL conic flask supports (total of sixteen slots) was used for sample preparation.

2.2. Instrumental parameters

The optimised instrumental parameters are described below. For the MIP-OES (Table 1), the optical parameters were adapted based on wavelengths 606.424 and 530.455 nm. A T-piece was used to inject the sample and the forming-reactant into the spray chamber at the same time. The pump parameters were improved to achieve a stable injection and avoid high pressure in the tubes. Moreover, the uptake and stabilisation times were optimised based on the instrument set-up.

For HR-GF MAS, the results were obtained based on the method described by Akhdhar et al. [18] but no permanent modifier was used. Calcium was used as the forming reagent and the temperature program applied is described in Table 2.

2.3. Chemicals

Ultrapure water with a resistivity of 18.2 MΩ cm (Smart2 Pure, Thermo Fisher Scientific, UK) was used for sample dilution and preparation of calibration solutions. Potassium fluoride, KF (Fishers Scientific, Waltham, MA, US) was used as the forming reagent. For HR-GF MAS, 99.998% purity argon gas was provided by BOC (Dublin, Ireland).

2.4. Samples and sample preparation

A selection of seven tea samples of different brands from the local market in Aberdeen, United Kingdom and three different brands of tea samples from Saudi Arabia were used in this study. Tea infusion samples were prepared to simulate the preparation of tea for daily use. Approximately 15 mL of water at 90°C was added to 0.15 g of tea in a falcon flask and then left to brew for 5 min. In the next step, the mixture was centrifuged (5 min, 3000 rpm) and the supernatant extracted.

3. Results and discussions

3.1. Wavelength selection

Currently, there is no report about instrumental conditions for fluorine determination via CaF using MIP-OES instruments or any molecular mass spectrometry (HR-GF MAS).

| Table 1 | Optimised instrumental parameters for total fluorine determination via CaF using MIP-OES instruments or any molecular mass spectrometry (HR-GF MAS). |
|---------|----------------------------------------------------------------------------------------------------------|
| Description | Value |
| Wavelength used | 530.455 nm |
| Peristaltic pump speed | 15 rpm (revolutions per minute) |
| Fast pump | off |
| Viewing position | 240° |
| Nebulizer pressure | 100 kPa |
| Volume flow rate (Ca) | 1.4 mL min$^{-1}$ |
| Sample uptake time | 25 s |
| Stabilisation time | 15 s |

*Arbitrary number from the software.*
optical emission spectrometry technique. For this reason, it was necessary to evaluate the best wavelengths and conditions, examining not only sensitivity (signal to noise ratio), but also the absence of spectral interferences. All spectra were recorded using NaF or KF and HF to ignore possible Na and K lines. According to Pearse and Gaydon [19], the suggested transition wavelengths were scanned with a ± 0.25 nm range: 330.9, 529.9, 606.5, 685.6, 703.7 and 720.2 nm. Selected scans using different total fluorine concentrations are illustrated in the supplementary material (Figure S1-S8). The CaF molecule has a strong emission in the range of 605.5–606.7 nm, where the most intense band head is at 606.424 nm (Fig. 1).

This line was used for optimisation of nebulizer pressure (effectively nebulizer gas flow) and observation height (see Fig. 2 and S9). While the nebulizer gas flow has a negligible effect, the CaF signal to noise ratio shows large variability in the observation height. Deep in the plasma there is no sensitivity, the signal increased with distance from the torch. The signal stayed reasonably stable in the tail of the plasma. All other lines show similar patterns. This suggests that CaF is formed and excited in the cooler area of the plasma.

Another area of the spectrum also showed strong emission lines between 529.2 and 530.5 nm which are used in molecular absorption spectrometry [20]. Fig. 3 shows the concentration dependent wavelength scan of the spectrum (529 nm is shown in Figure S10). Most other lines were not useful for total fluorine determination due to low sensitivity.

### Table 2

| Step           | T/°C | Ramp/°C s⁻¹ | Hold/s |
|----------------|------|-------------|--------|
| Drying 1       | 80   | 6           | 15     |
| Drying 2       | 110  | 5           | 20     |
| Pyrolysis      | 900  | 300         | 10     |
| Molecule formation | 2300 | 3000        | 5      |
| Cleaning       | 2450 | 500         | 4      |

Fig. 2. Observation height optimisation of the CaF at 606.424 nm using 1000 mg L⁻¹ fluorine. Observation height measured in arbitrary units; increasing number increases height above the torch.

Fig. 3. Spectral emission profiles of the CaF molecule between 529.3 nm and 530.7 nm. The profile was generated by a 10–1000 mg L⁻¹ solution of total fluorine and 20 g L⁻¹ of calcium. The lines 529.293 and 530.455 nm were used for further optimisation and calibrations. * lines were used for calibration.

### 3.2. Optimisation of reagent-forming concentration

In order to investigate whether chloride from CaCl₂ and potassium from KF had an influence on the occurrence of the observed lines, Ca(NO₃)₂ and NaF and HF were used as reagents and the lines were characteristic for CaF. No significant effect was identified. Hence, the line was not generated by K.

For this study, solutions with concentrations of up to 30 g L⁻¹ of Ca were used as forming reagent, while a standard aqueous solution of 50 mg L⁻¹ of fluoride using 530.455 nm line was employed. The results displayed in Fig. 4 show a clear increase of the analytical signal in concentrations up to 20 g L⁻¹. For concentrations between 20 g L⁻¹ to 30 g L⁻¹, the sensitivity enhancement was not significant. To avoid an excess of calcium causing deposition in the torch, the concentration of 20 g L⁻¹ was chosen as optimal and adopted for the calibration and measurement of tea infusions.

### 3.3. Figures of merit and accuracy evaluation

The different lines were used for calibration between 10 and 1000
mg L\(^{-1}\) total fluorine. The signal shows that a linearity over two orders of magnitude could be found for three lines (530.455 nm, 529.293 nm, and 606.424) which are shown in Fig. 5 and S11 and S12).

The R\(^2\) was 0.99 for the tested 529.293 and 530.455 nm lines. The limits of detection (LOD) and quantification (LOQ) were calculated by 3 and 10 times the standard deviation of 10 measurements of a blank solution, divided by the angular coefficient of the calibration curve. The obtained results are shown in Table 3 with only the 530.455 nm line in comparison to the figures of merit of the reference method for total fluorine, HR-GF MAS. This illustrates that the MIP-OES method is not as sensitive and precise than the reference method, but it has a greater dynamic concentration range up to high concentrations.

### 3.4. Application of MIP-OES to tea infusions and validation approach

The MIP-OES is not good enough for the testing of water samples, since the LOQ is above the WHO guideline for fluoride in drinking water. But MIP-OES was chosen to test for accuracy and precision when measuring fluorine rich real samples, here tea infusions. Since no certified reference material for total fluorine in tea infusion was available, the real samples were also measured with a complimentary method, which has been used previously for the quantification of total fluorine in tea infusions (HR GF MAS [20]); this was treated as a reference method. The results for the 10 different tea infusion samples are displayed in Table 4.

The concentrations of total fluorine in tea infusions in this study (2.7–7.8 mg L\(^{-1}\)) are similar to those of Chan et al. [10] who determined a fluoride concentration in a range of 0.43–8.8 mg L\(^{-1}\). They also recorded concentrations of fluoride from 2.3 to 6.2 mg L\(^{-1}\) in a green tea infusion, which was similar to those found in this study (4.7 mg L\(^{-1}\)). All samples were above the maximum WHO recommended level for fluoride in drinking water (<1.5 mg L\(^{-1}\)) [21–23].

Both techniques (MIP-OES and HR-GF MAS) showed similar concentrations of total fluorine. The concentration in the studied tea samples were found between <3.8 and 7.8 mg L\(^{-1}\). Using a paired Student's t-test (two tailed) to compare the two sets of results of total fluorine in black and green tea respectively measured using MIP-OES and HR-GF MAS showed no significant difference (P = 0.97), which means it is possible to measure total fluoride in tea using a commercially available MIP-OES. However, the precision measured in standard error of triplicate measurements shows that the MIP-OES method has a significantly higher in the real samples (28%) compared to HR-GF MAS (1.7%). This is due to the low concentration measured in the tea infusion close to its LOQ. The average recovery gives 97.8% of the MIP-OES data compared to HR-GF MAS. The average recovery gives 97.8% of the MIP-OES data compared to HR-GF MAS.

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Fluoride can easily be measured by ion selective electrode or ion chromatography in natural waters but have problems with more challenging matrices. However, these techniques are fluoride specific and other fluorine containing compounds, especially organofluorines, detrimental for human health cannot be measured with those techniques. They also do not have the potential to be coupled with a chromatographic technique which could allow for organofluorine speciation.

### 4. Conclusion

Commercially available MIP-OES has been used for the first time to
measure total fluorine using the formation of CaF in the plasma and measuring at 530.455 nm. The method is sensitive enough to measure total fluorine in tea infusions. The results are comparable with the results produced by the reference method. The precision of the method should be improved by further optimisation.

Credit author statement

E.K. and J.F. designed the experiment. M.S. A.A., S.H. and A.O. did the experimental work with the MIP-OES and the HR GF MAS. E.C. supervised M.S., J.F. and E.K. supervised A.A., S.H. and A.O. All participated in writing the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

A.A. would like to thank the Ministry of Education and University of Jeddah in Saudi Arabia for their financial support during the study period. M.S. would like to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq for the financial support. S.H. would like to thank the Ministry of Education and University of Jeddah in Saudi Arabia for their financial support during his research stay. A.O. would like to thank the Royal Society of Chemistry Analytical Chemistry Trust Fund for funding.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2021.122190.

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