



New analytical method for total fluorine determination in soil samples using high-resolution continuum source graphite furnace molecular absorption spectrometry



Wiliam Boschetti^a, Morgana B. Dessuy^{a,b,*}, Antônio H. Pizzato^a, Maria Goreti R. Vale^{a,b}

^a Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970 Porto Alegre, RS, Brazil

^b Instituto Nacional de Ciência e Tecnologia do CNPq–INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil

ARTICLE INFO

Article history:

Received 30 September 2016

Accepted 3 October 2016

Available online 05 October 2016

Keywords:

CaF diatomic molecule

Soil samples

HR-CS GF MAS

Direct analysis of solid samples

ABSTRACT

Fluorine may be present in soil naturally, in the form of minerals (fluorite, fluorapatite and cryolite) or due to environmental pollution. Plants harvested in soils with high levels of this element might be contaminated and consequently they may present toxicological effects, such as necrosis or growth reduction. Hence, the development of reliable and appropriate methods for the accurate determination of F has become of great importance. The aim of this study was the development of an analytical method for F determination in soil samples, monitoring the rotational lines of the CaF molecule by high-resolution continuum source graphite furnace molecular absorption spectrometry using direct analysis of solid samples. All measurements were carried out using the wavelength at 606.440 nm, evaluating the center pixel only, and a standard solution of 7.5 g L⁻¹ Ca was used as the molecule-forming reagent. The pyrolysis and atomization temperatures were optimized to 900 °C and 2100 °C, respectively; the Ca mass of 75 µg was adequate to guarantee the formation of the CaF molecule in samples and standard solutions. Sample masses up to 0.25 mg were weighted. Fluoride aqueous standard solutions were used for calibration, resulting in a linear working range between 1.5 and 27 ng F. The characteristic mass obtained was 0.13 ng and the limits of detection and quantification were 0.72 and 2.4 ng mg⁻¹, respectively, calculated for a sample mass of 0.25 mg. A certified reference material of Lake Sediment (LKSD-4, Ontario, Canada) was used to confirm the trueness of the developed method. The value found for F (234 ± 14 ng mg⁻¹) was in agreement with the certified value (260 ± 40 ng mg⁻¹), proving that the developed method provides accurate results for F determination in soil samples. Finally, the developed method was applied for the analysis of soil samples from urban and rural areas. Considering all the investigated soil samples, the F content varied between 138 and 232 ng mg⁻¹.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Fluorine is the 13th element most abundant in nature, present in about 0.09% of the Earth's crust [1]. It can be found in mineral rocks, especially as fluorite (CaF₂), fluorapatite (Ca₁₀(PO₄)₆F₂) and cryolite (Na₃AlF₆) [2]. On the other hand, the main anthropogenic sources of F are the gaseous emissions from aluminum smelters, coal power plants, brick and cement manufacturers, chinaware and glassware factories, and phosphate manufacturing plants [3]. The natural fluorine content in the soil vary between 10 and 500 mg kg⁻¹, however, these concentrations can increase significantly if the soil was fertilized through a long period with phosphates, as soil amendment, or if it is situated in the vicinity of aluminum smelters, coal power plants or cement industries [2–5].

In plants, fluorine and fluorides are known to be potentially toxic; their compounds are absorbed through the roots and/or leaves [6,7]. From the soil, these substances are transferred from roots to the respiratory organs (leaves), via xylematic flow, where they are usually accumulated [8–10]. The typical symptoms, attributable to F pollutants, consist in tip and margin necrosis ('tip burn') of the leaves [11,12]. Moreover, the F amount that may cause these injures depends on the plant species, varying from 50 to 2000 mg kg⁻¹ [13–16].

For humans, high F amounts can cause several health problems: gastric disorders, temporary reduction of urinary capacity, dental or skeletal fluorosis and even death, depending on the dose, time of ingestion and age [17,18]. Fluorine is usually uptake from drinking water and food (plants and animals) [19,20]. Soils presenting high F concentrations can be considered a contamination source for drinking water [2, 21,22]. Thus, analytical methods that can provide fast and reliable results are vital in order to control F contaminations in soils.

Literature reports that F is usually determined using an ion-selective electrode, which provides the measurement of free and complex-bound

* Corresponding author at: Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970 Porto Alegre, RS, Brazil.

E-mail address: mbdessuy@ufrgs.br (M.B. Dessuy).

fluoride dissolved in water [22,23]. Others techniques that can be used to perform F determination are ion chromatography and atomic and molecular spectrometry [23]. Most of the cited techniques require a sample pretreatment step. In this context, the use of the high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS) can be an effective alternative technique since it allows the direct analyses of solid samples [24–26]. Therefore, it provides F quantification with a minimum pretreatment, avoiding sample dilution or contamination.

It is well known that F can be determined by HR-CS MAS via different diatomic molecules: CaF, GaF, AlF, SrF [27–43]. For example, Borges et al. [37] determined F in plant material via CaF diatomic molecule by HR-CS GF MAS using direct analysis of solid samples. Huang et al. [27] succeeded in quantifying the F content, in a super-phosphate certified reference material (CRM), via the GaF molecule using an air-acetylene flame. Ozbek and Akman [32], in 2012, using the absorption of the AlF molecule, determined F in toothpaste in a nitrous oxide–acetylene flame. Ozbek and Akman [33], in 2012, also investigated the absorption of the SrF molecule without modifier for the determination of F in water samples by HR-CS GF MAS; however a relatively high detection limit was obtained.

In this work, the CaF molecule with a resonant line at 606.440 nm was chosen for F determination in soil samples. One of the CaF advantages is that calcium acts both as the molecule-forming reagent and as a chemical modifier. Another advantage is the minimum risk for spectral interferences at the selected wavelength, as only a few atoms have absorption lines nearby. Therefore, the main objective of the present work was to develop an analytical method and investigate its applicability on the determination of F via the molecular absorption of CaF in different soil samples, using HR-CS GF MAS and direct analysis of solid samples.

2. Experimental

2.1. Instrumentation

All measurements were performed in a high-resolution continuum source atomic absorption spectrometer Model contrAA 700 (Analytik Jena AG, Jena, Germany). This equipment contains a xenon short-arc lamp, with a nominal power of 300 W, a compact high-resolution double monochromator, which consists of a prism and an echelle grating and a charge-coupled device (CCD) detector. Considering that the Xe lamp emits continuum spectra between 190 and 900 nm, it was possible to determine F via its diatomic molecule, CaF, at the resonance line of 606.440 nm. The integrated absorbance (A_{int}) values were obtained by measuring the peak area of the center pixel (CP) only.

Solid sample (SS) graphite platforms (Analytik Jena, Part no. 407-152.023) and pyrolytically coated transversely heated graphite furnaces without dosing hole (Analytik Jena, Part no. 407-A81.303) were used in all experiments. 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 the vaporization where the gas flow rate was stopped. A MSA6.6S-000-DM microbalance (Sartorius, Göttingen, Germany) was used to weigh the soil samples onto the SS platform and a SSA 5 manual solid sampling accessory (Analytik Jena, Jena, Germany), with a pre-adjusted pair of tweezers, was used to transfer the platform to the atomizer. The optimized graphite furnace temperature program used for fluorine determination in soil samples is shown in Table 1.

2.2. Reagents

All analytical solutions were prepared using ultrapure water obtained from a Milli-Q system (Millipore, Bedford, MA, USA). All used containers were soaked in 1.4 mol L⁻¹ nitric acid for 24 h and washed three times with ultrapure water and placed in a laminar flow hood to

Table 1

Temperature program for F determination (via CaF molecule) in soil samples by HR-CS GF MAS using direct analysis of solid samples.

Stage	Temperature/°C	Ramp/°C s ⁻¹	Hold time/s
Drying 1	90	5	20
Drying 2	140	5	20
Pyrolysis	900	500	30
Vaporization	2100	3000	10
Cleaning	2500	1000	4

dry. Calcium was employed as the molecule-forming reagent and all Ca solutions were prepared using the calcium nitrate salt Ca(NO₃)₂·4H₂O (Vetec, Duque de Caxias, Brazil) in the presence of 0.05% (v/v) Triton X-100 (Sigma-Aldrich, St. Louis, Missouri, USA). The fluorine standard solutions were prepared from the sodium fluoride salt NaF (Merck, Darmstadt, Germany).

2.3. Procedure and sample preparation

Soils from urban and countryside areas were investigated. Six soil samples (R1–R6) were obtained from the rural area of Pinto Bandeira (Rio Grande do Sul, Brazil). These samples were randomly collected in different spots in a 10.000 m² vineyard field. The urban soil samples (U1–U3) were gathered at Porto Alegre (Rio Grande do Sul, Brazil) urban center. These samples were obtained from three different sites: two samples were picked up next to busy roads and one nearby to a cement industry. After collected, all samples were dried in a dark room, protected from the wind and stored in plastic bags. All soil samples were submitted to a grinding process in an agate mortar and then sieved through a 200 µm polyester sieve and kept in sealed plastic vials until analysis.

Taking into account the analysis procedure, each soil sample was weighed directly onto the SS platform and, before being introduced into the graphite furnace, 10 µL of 7.5 g L⁻¹ Ca solution in the presence of 0.05% (v/v) Triton X-100 were pipetted over the sample. It was weighed masses between 0.05 mg and 0.25 mg for all investigated samples. Since the sample mass was different for each measurement, the A_{int} was normalized for an appropriated sample mass for comparison. A certified reference material (CRM), Lake Sediment – LKSD-4 (NRCAN, Ontario, Canada) was evaluated in order to confirm the trueness of the developed method.

3. Results and discussions

3.1. Molecule-forming reagent and soil sample mass evaluation

To guarantee that all F present in the samples and standard solutions was converted into the CaF diatomic molecule, the Ca amount required was investigated. For this purpose, it was investigated the effect of different Ca masses (15–150 µg), over the CaF A_{int} values, evaluating a soil sample and a F aqueous standard solution (Fig. 1). To achieve these Ca masses, 10 µL of different standard solution, with Ca concentration between 1.5 and 15 g L⁻¹, were pipette over the weighed samples. Fig. 1 shows that for the F standard solution in the absence of Ca, the CaF molecule formation did not occurred ($A_{int} = 0.00524$). Increasing the Ca mass added over the standard solution, the CaF molecule started to be formed and its A_{int} values reached a plateau for Ca masses higher than 30 µg.

Considering the soil sample (U3), a CaF analytical signal was obtained ($A_{int} = 0.0314$) even without Ca addition, probably due to the presence of this element in the sample. It is also possible to observe that employing 75 µg Ca, the highest CaF A_{int} values were obtained. For both, standard and sample, the use of higher Ca mass did not increase the CaF A_{int} values, indicating that all F present in sample and standard was converted into the CaF molecule using 75 µg Ca.

Download English Version:

<https://daneshyari.com/en/article/7641217>

Download Persian Version:

<https://daneshyari.com/article/7641217>

[Daneshyari.com](https://daneshyari.com)