



Determination of fluorine in milk and water via molecular absorption of barium monofluoride by high-resolution continuum source atomic absorption spectrometer



Nil Ozbek*, Suleyman Akman

Istanbul Technical University, Faculty of Arts and Sciences, Department of Chemistry, 34469 Maslak, Istanbul, Turkey

ARTICLE INFO

Article history:

Received 14 May 2014

Received in revised form 9 June 2014

Accepted 11 June 2014

Available online 19 June 2014

Keywords:

High-resolution continuum source electrothermal atomic absorption spectrometry

Molecular absorption spectrometry

Fluorine

Barium monofluoride

Water

Milk

ABSTRACT

This study describes the determination of fluorine evaluating the molecular absorption of barium monofluoride (BaF) at the rotational lines of 495.088 and 495.263 nm simultaneously using a high-resolution continuum source electrothermal atomic absorption spectrometer. Upon pipetting of samples together with Ba as its nitrate, BaF was generated in the gas-phase of the atomizer. All experiments were performed using pyrolytically coated graphite tubes/platforms and applying 900 °C for pyrolysis and 2200 °C for vaporization. In the presence of 50 µg of Ba, a perfect linearity up to 0.1 µg of F was maintained. The limit of detection and characteristic mass of the method were 0.105 ng and 0.055 ng of F, respectively. The F concentration of a standard waste water sample was found in the uncertainty limits of its certified value as well as spike additions were quantitatively recovered. Finally, F concentrations in various water and milk samples sold in markets were determined.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Fluorine can be listed as the most electronegative and one of the most reactive elements. It is generally known for its key health benefit, preventing dental decay. It also takes part in many metabolic processes in the body. However, it is only helpful when used in small amounts. In the long term, excess exposure to fluorine can cause cancer, dental fluorosis and bone fractures [1,2]. Personal fluorine ingestion should be kept between 2 and 3 mg per day. If the amount taken by fluoridated drinking water, toothpaste and food exceeds 20 mg a day for 10 or more years, it would lead to a significant risk for bone health [3].

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 have been well reviewed by Huang et al. [4]. The usual determination methods of fluorine are potentiometry (fluoride ion selective electrodes) [5], spectrophotometry [6], ion chromatography [7] and capillary electrophoresis [8]. Ion selective electrodes are easy to use and cost effective however it responses are only to free F ions in the aqueous phase and also require constant ionic strength and pH control. Potentiometric (ion selective electrode) and ion chromatographic methods are not suitable only for the determination of organic or covalently bond fluorine. Since fluorine is the most electronegative element with very high ionization potential of

17.42 eV, and its resonance lines are located in the vacuum UV range below 100 nm, spectrometric methods like inductively coupled plasma atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS) are not feasible for fluorine determination. Besides, inductively coupled plasma mass spectrometry (ICP-MS) is also not suitable for the determination of fluorine because the ionization potential of the argon plasma is not sufficient to ionize this element [9]. Hence, photometric methods are suitable only to ionic fluoride in aqueous systems whereas HPLC or LC-MS can be used for molecular forms of F and require appropriate standards (if species detected are absent in the library of the instrument).

Atomic absorption spectrometry (AAS) is a traditional analytical technique for quantitative determination of trace metals and metalloids. The traditional LS-AAS (line source atomic absorption spectrometry) cannot be used for the determination of fluorine because the main resonance line of F is located at 95 nm which cannot be instrumentally applied. There are some efforts for the determination of fluorine with line source AAS using an HCL of an element that emits a line that coincides with the absorption spectrum of the molecule of interest. For this purpose, upon addition of a suitable molecule forming element, the diatomic molecules of the analytes were generated in the gas phase. The molecular absorption for the diatomic molecules at one of its fine rotational lines was measured using any suitable hollow cathode lamp (HCL) [10–13]. However, the exact overlapping emission line of the selected HCL with a very narrow line of diatomic molecule at rotational level is not possible and some drift may occur, which causes

* Corresponding author. Tel.: +90 2122853160; fax: +90 2122856386.
E-mail address: nil.ozbek@itu.edu.tr (N. Ozbek).

low sensitivity along with spectral interferences. As a result, the studies for the determination of F by line source AAS have become marginal.

On the other hand, high resolution continuum source atomic absorption spectrometers (HR-CS AAS) are appropriate to measure the molecular absorption of diatomic molecules at one of their fine rotational lines [14]. Therefore, for the determination of non-metals, the problems with line source AAS (LS AAS) do not occur in HR-CS AAS. Total fluorine (organic and inorganic, free and covalently bond) in all solvents (aqueous and organic) can be determined [15]. Without a doubt, HR-CSAAS is an expensive instrument but if there is an AAS in the laboratory, it can be effectively used for routine determination of F with the above-mentioned advantages.

There are some studies for the determination of fluorine by HR-CS AAS using molecular absorption of several diatomic molecules like AlF, GaF, CaF and SrF [9,15–21]. Welz et al. and Butcher reviewed the fluorine determinations performed by LS AAS and HR-CS AAS, thoroughly [22,23]. However, Ba has not been used as a molecule forming element for the determination of fluorine by HR-CS AAS. Barium was successfully used for the determination of iodine via the spectrum of barium monoiodide using high-resolution continuum source molecular absorption spectrometry in a graphite furnace but has not been applied for the determination of fluorine before [24].

In this study, for the first time, Ba was used as a new molecule forming element for the determination of fluorine in drinking water and milk samples via molecular absorption of barium mono-fluoride (BaF) by high-resolution continuum source molecular absorption spectrometry (HR-CS MAS) in a graphite furnace. In order to reduce the LOD and characteristic mass, the BaF signals observed on the same window were summited. The experimental and instrumental parameters were optimized and figures of merit were determined.

2. Experimental

2.1. Instrumental

Graphite furnace mod of an Analytik Jena ContraA 700 high resolution continuum source atomic absorption spectrometer equipped with a 300 W xenon short arc lamp (XBO 301, GLE, Berlin, Germany), high resolution double monochromator consisting of a prism, an echelle monochromator and a charge-coupled device (CCD) array detector was used for all measurements. The resolution ranges from 1.6 pm per pixel at 200 nm, to about 6.4 pm at 800 nm. All measurements were made at 495.088 and 495.263 nm simultaneously with 3 + 3 pixels (central pixel ± 1) and using pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025). The summation of the absorbances at the two wavelengths was evaluated.

2.2. Reagents and solutions

In all dilutions, a high-purity water (resistivity 18.2 M Ω ·cm) was used which was obtained by a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungssysteme GmbH, Niederelbert Germany). Inorganic acids and reagents were analytical grade (HNO₃, 65% (w/w), Merck, Darmstadt, Germany). The fluorine standard was prepared from sodium fluoride (Merck, Darmstadt, Germany). A stock solution of 10,000 mg L⁻¹ Ba was prepared from barium nitrate (Merck, Darmstadt, Germany). Pd (0.2% Pd in 5% HNO₃) and Pd–Mg (0.3% Pd + 0.5% Mg in 1% HNO₃) solutions (SCP Sciences, Courtaboeuf, France) were used to test the effect of modifier on the results. The stock solutions of Zr and Ir were prepared from nitrate forms (Merck, Darmstadt, Germany). The waste water standard reference material SPS-NUTR-WW2 was provided from LGC Standards (Middlesex, England). Various drinking water and milk samples were obtained from markets in Turkey.

2.3. Procedure

Fluorine was determined via the rotational molecular absorption line of diatomic BaF at 495.088 nm using HR-CS ET AAS. Samples (or standard solutions) and then 5000 $\mu\text{g mL}^{-1}$ of Ba as the nitrate were pipetted one after another as 10 μL . The optimized graphite furnace temperature program is given in Table 1. In order to cover the surface of the platform with zirconium or iridium, 20 μL of 1000 $\mu\text{g mL}^{-1}$ Zr or Ir as the nitrate was pipetted, dried and thermally treated at 1100 °C for 10 s. The procedure was repeated 5 times [16].

3. Results and discussion

Actually, the formation of diatomic molecules is a well known interference mechanisms in determinations by ET AAS and not preferred whereas it is necessary and supported for the determination of non metals via their diatomic molecules. The formation mechanisms of SrF were extensively studied and clarified by Ozbek and Akman [25]. By analogy, the formation mechanisms of BaF may be proposed as follows: It can be expected that BaF₂ is formed prior to the volatilization step. BaF₂ is decomposed to form Ba and F atoms in the gas phase which are then recombined to form BaF. Similar mechanisms were proposed for the gas-phase interference mechanisms of many metals and halogens (especially chlorine). BaF₂ may remain in the furnace in the drying and pyrolysis steps and then volatilize directly in the volatilization step and then BaF may form upon separation of one F from BaF₂. The theoretical evaluation given above was added to the text upon basic comment of the reviewer. Nevertheless, only theoretical evaluation was made but further speculations were over-estimated.

3.1. Choice of molecule forming element and the working wavelength

The method is based on the formation of a diatomic molecule between the analyte and an element (molecule forming element) and measurement of the molecular absorption at one of its rotational lines. For this purpose, the samples or standards and then a molecule forming element were injected in the furnace to form a diatomic molecule of the analyte in the gas phase and then molecular absorption at a line selected from its electron excitation spectrum with rotational fine structure, is measured. The diatomic molecule of F formed in the gas phase should be stable enough so that the chosen diatomic species should have bond dissociation energies above 500 kJ mol⁻¹ [9]. The whole procedure is expected to be simple, needing minimum or no auxiliary reagent(s) and no extra pretreatment of the furnace.

In the spectral range of the instrument, the possible wavelengths for BaF are found as 500.066, 499.216, 495.088, 495.266 nm according to Pearse and Gaydon [26]. The most sensitive two wavelength-resolved molecular absorption spectra for BaF are depicted in Fig. 1. As shown in the figure, the most sensitive line was 495.088 nm. In the same window, another BaF line of 495.263 nm can be detected. In order to enhance the sensitivity and thereby to reduce the limit of detection (LOD) and characteristic mass (m_0), the summation of the two wavelengths

Table 1

The graphite furnace temperature–time program optimized for the determination of F from MAS of BaF at 495.088 nm and summation of absorbances at 495.088 and 495.263 nm.

Step	Temperature (°C)	Ramp (°C s ⁻¹)	Hold time (s)	Gas flow (L min ⁻¹)
Drying	80	6	20	2.0
Drying	90	3	20	2.0
Drying	120	5	10	2.0
Pyrolysis	900	300	10	2.0
Gas adaption	900	0	5	Stop
Molecule formation	2200	2000	5	Stop
Cleaning	2500	500	4	2.0

Download English Version:

<https://daneshyari.com/en/article/7642874>

Download Persian Version:

<https://daneshyari.com/article/7642874>

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