Talanta 94 (2012) 246–250

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Method development for the determination of fluorine in toothpaste via molecular absorption of aluminum mono fluoride using a high-resolution continuum source nitrous oxide/acetylene flame atomic absorption spectrophotometer

Nil Ozbek, Suleyman Akman*

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

ARTICLE INFO

Article history:
Received 2 January 2012
Received in revised form 15 February 2012
Accepted 22 March 2012
Available online 28 March 2012

Keywords:
Fluorine
Aluminum
Toothpaste
High resolution continuum source flame atomic absorption spectrometry

ABSTRACT

Fluorine was determined via the rotational molecular absorption line of aluminum mono fluoride (AlF) generated in C_2H_2/N_2O flame at 227.4613 nm using a high-resolution continuum source flame atomic absorption spectrophotometer (HR-CS-FAAS). The effects of AlF wavelength, burner height, fuel rate (C_2H_2/N_2O) and amount of Al on the accuracy, precision and sensitivity were investigated and optimized. The Al–F absorption band at 227.4613 nm was found to be the most suitable analytical line with respect to sensitivity and spectral interferences. Maximum sensitivity and a good linearity were obtained in acetylene-nitrous oxide flame at a flow rate of 210 L h^{-1} and a burner height of 8 mm using 3000 mg L^{-1} of Al for 10–1000 mg L^{-1}of F. The accuracy and precision of the method were tested by analyzing spiked samples and waste water certified reference material. The results were in good agreement with the certified and spiked amounts as well as the precision of several days during this study was satisfactory (RSD < 10%). The limit of detection and characteristic concentration of the method were 5.5 mg L^{-1} and 72.8 mg L^{-1}, respectively. Finally, the fluorine concentrations in several toothpaste samples were determined. The results found and given by the producers were not significantly different. The method was simple, fast, accurate and sensitive.

1. Introduction

Fluorine is a natural element which is found abundantly in world crust. Like various elements, fluorine is also required in the body but in small amounts. It is essential for human body in a very small critical concentration range and many harmful effects occur in case of its excess or deficiency. Fluorine is helpful for dental health in low dosage and added to many dental products like toothpastes, mouth rinses, gels and varnish as active ingredient. However, chronic exposure to fluoride in large amounts interferes with bone formation and can cause skeletal fluorosis, hence the amount of fluoride intake is very important [1].

There are numerous methods for determining fluorine and fluorine forms in toothpastes such as analytical methods [2], ion-selective electrodes [3,4], potentiometric determination [5], ion chromatography [6], spectrophotometric methods [7] and capillary electrophoresis [8] while each of them have their own disadvantages. There are some extraordinary studies about determining fluorine in toothpastes with atomic absorption spectrometry [9,10]. Gomez et al. formed gaseous AlF molecule in nitrous oxide–acetylene flame and measured its absorption by Pt hallow cathode lamp's absorption line. Method's sensitivity is very low (around 60 mg L^{-1}) because of line source spectrometer, hence it enables the determination of low concentrated fluorine samples [9].

Atomic absorption spectrometry (AAS) has been a routine analytical method for quantitative determination of trace metals and metalloids for years but with recent developments in high-resolution continuum source atomic absorption spectrometry, halogens and sulphur can be determined as well. It is impossible to determine fluorine directly by traditional line source spectral lamp since its main resonance line is located at 95 nm. With traditional AAS, some studies have been performed for the determination of fluorine which are well reviewed in literature [11]. In order to achieve these kinds of studies, diatomic molecules of fluorine in gas phase were generated by adding some metals. The absorption of a suitable hyperfine rotational line selected from the molecular absorption spectrum (MAS) of diatomic molecule was evaluated using corresponding emission line of any hollow cathode lamp (HCL). However, this method has some drawbacks: (i) a suitable HCL may not always be found, (ii) selected HCL's emission line may not exactly overlap with MAS line of diatomic molecule

---

* Corresponding author. Tel.: +90 2122853160; fax: +90 2122856386.
E-mail address: akmans@itu.edu.tr (S. Akman).

0039-9140/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.03.034

causing low sensitivity as well as spectral interference. On the other hand, high resolution continuum source atomic absorption spectrometer (HR-CS-AAS) with high intensity xenon short-arc lamp, high resolution double monochromator, CCD detector [12], it is possible to get whole wavelength range from vacuum-UV to near IR with a line width of 2 pm which is narrower than that of HCL as well as any line of rotational hyperfine structure of the diatomic molecule. In this case, the above mentioned drawbacks of HCL do not occur. Many studies have been performed for the determination of fluorine by HR-CS-AAS using any rotational molecular absorption line of GaF, AlF, MgF and CaF [13–19].

The aim of this study is to develop a novel method for the determination of F in toothpaste samples by HR-CS-AAS using molecular absorption line of AlF formed in acetylene–nitrous oxide flame. The experimental parameters were optimized and the method was validated. To the best of our knowledge, this is the first time that aluminum is used as a molecule forming element for the determination of F in flame by high-resolution continuum source atomic absorption spectrometry.

2. Experimental

2.1. Instrumental

An Analytik Jena ContrAA 700 High Resolution Continuum Source Atomic Absorption Spectrophotometer (Analytik Jena, Jena, Germany) equipped with a 300 W xenon short-arc lamp as a continuum radiation source was used throughout the work. AlF was formed in acetylene-nitrous oxide flame with a flow rate of 210 L h^{-1}. The molecular absorption measurements of AlF were carried out at 227.4613 nm and at a burner height of 8 mm. The number of pixels of the array detector used for detection of AlF line was 1 (central pixel). All measurements were carried out in triplicates. In order to prepare samples, ultrasonic bath (Bandelin Sonorex, Waldorf, Germany) has been used.

2.2. Reagents and solutions

High-purity water was obtained from a TKA reverse osmosis connected with a deionizer (TKA Wasseraufbereitungsysteme GmbH, Niederelbert Germany). All chemicals were of Merck, Darmstad, Germany). The stock solutions of 5000 mg L^{-1} of fluorine and 10,000 mg L^{-1} aluminum standards were prepared by dissolving high purity sodium fluoride and aluminum nitrate (Merck, Darmstad, Germany) in water and further diluted daily appropriately. The waste water standard reference material SPS-NUTR-WW2, which includes 10.0 ± 0.1 mg L^{-1} of F^-, 50.0 ± 0.5 mg L^{-1} of Cl^-, 7.5 ± 0.08 mg L^{-1} of $PO_4{}^{3-}$, 5.0 ± 0.05 mg L^{-1} of $NO_3{}^-$and 100 ± 1 mg L^{-1} of $SO_4{}^{2-}$, was provided from LGC Standards (Midlesex, England). Six different brands of toothpaste samples containing sodium fluoride and sodium monofluorophosphate were purchased from market in Istanbul, Turkey.

2.3. Procedure

Matrix-free standard solutions of fluorine, waste water reference standard and blanks were mixed with aluminum 3000 mg L^{-1} as the molecule forming element and aspirated to the flame at optimized conditions. Blank solution was 3000 μg mL^{-1} Al as the nitrate. In order to prepare the toothpaste solution (or suspension), 1 g of sample was precisely weighed, dispersed in ultra pure water and completed to 50 mL again with ultra pure water. The mixture was homogenized in ultrasonic bath at 50 °C for 30 min and an aliquot of 5 mL was then immediately made up to 10 mL with 6000 μg mL^{-1} of Al as the nitrate. In spite of an effective ultrasonic homogenization, the samples slowly precipitated upon waiting. Therefore, the mixture was vortexed for about 1 min prior to aspiration in to the flame. The samples were introduced as their suspensions (or dilute slurries). The slurry was diluted to a certain level that it was aspirated like a solution without any problem (e.g. without clogging or deposition in the burner head and aspiration capillar tube). The results were given as the mean of 3 repetitive aspiration of each sample.

3. Results and discussion

3.1. Choice of molecule forming element

In this method a diatomic molecule is formed in the flame among the analyte and an element (molecule forming element) and MAS of the molecule is measured. The element is chosen so that the diatomic molecule containing the analyte should be stable enough to stay in the flame during the measurement while its sensitivity is sufficient for the detection of the analyte concentrations (strictly speaking the concentration of diatomic molecule formed from the analyte) in the samples studied. It is assumed that diatomic species with bond dissociation energies higher than 500 kJ mol^{-1} are suitable for this purpose [16]. The dissociation bond energy of AlF is 653 kJ mol^{-1} [18]. Therefore, Al is an appropriate element for the determination of F. In addition, it is easily available and cheap. AlF may be formed by decomposition of AlF_3 ($AlF_3(g) \rightarrow AlF(g) + F(g)$) and/or recombination of Al and F atoms in the gas phase ($Al(g) + F(g) \rightarrow AlF(g)$). However, we do not make overestimations on the formation mechanisms of AlF(g).

3.2. Choice of calibration standard

The stock solution of fluorine was prepared from high purity sodium fluoride and HF. Optimization was done with two different fluorine reagents, and no significant difference was found between the sensitivities of the two standards. Since HF is risky for health and corrosive to flame parts of instrument, NaF was used as a calibrant.

3.3. Choice of wavelength

The wavelength of the analyte containing diatomic molecule is chosen such that its sensitivity is high enough to detect the analyte in the sample while the analyte absorption line does not spectrally interfere with neighboring wavelengths of other species. The spectral interferences in HR-CS-AAS are less likely compared to line source AAS as a result of extraordinary high resolution power of the former at pm level. Spectral interferences occured due to the overlapping of the two wavelengths (analyte and the species formed in the flame) can be corrected if and only if the source of the interference is known.

In the literature, F has been determined by molecular absorption of AlF at lines 227.5 [14], 277.45 [9], 227.438 and 227.485 [20] by hollow cathode lamps. Some other lines are listed for AlF by Pearse and Gaydon [21] as 227.4613, 227.4659, 227.5790, 227.6631 nm. All of these lines were investigated with respect to their sensitivities and spectral interferences and the highest absorbances were obtained at 227.4613 nm. The absorption spectra obtained for toothpaste in the vicinity of molecular absorption peak of AlF at 227.4613 nm is depicted in Fig. 1. In the toothpaste samples used in this work, the background is low and there is no spectral interference from close environment of molecular absorption peak of AlF at 227.4613 nm.

3.4. The effect of the amount of Al on the sensitivity

The linearity of the calibration curve for the determination of halogens via MAS of their diatomic molecules needs extra