



## Analytical Methods

# Solid sampling determination of total fluorine in baby food samples by high-resolution continuum source graphite furnace molecular absorption spectrometry



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## ABSTRACT

This study describes the applicability of solid sampling technique for the determination of fluorine in various baby foods via molecular absorption of calcium monofluoride generated in a graphite furnace of high-resolution continuum source atomic absorption spectrometry. Fluorine was determined at CaF wavelength, 606.440 nm in a graphite tube applying a pyrolysis temperature of 1000 °C and a molecule forming temperature of 2200 °C. The limit of detection and characteristic mass of the method were 0.20 ng and 0.17 ng of fluorine, respectively. The fluorine concentrations determined in standard reference sample (bush branches and leaves) were in good agreement with the certified values. By applying the optimized parameters, the concentration of fluorine in various baby foods were determined. The fluorine concentrations were ranged from <LOQ to 3.75  $\mu\text{g g}^{-1}$ . Owing to the ultra low sample amounts used in solid sampling analysis, micro-scale distribution of fluorine in the samples was also determined.

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## 1. Introduction

Fluorine is the most abundant halogen and the thirteenth most common element in Earth's crust. It prevents the dental cavities and improves the oral and bone health whereas excessive consumption may cause dental and skeletal fluorosis, leads to increased likelihood of bone fractures, and oxidative stress in the liver (Akman, Welz, Ozbek, & Pereira, 2015; U.S. Environmental Protection Agency, 2010). Fluorine may also cause increased insulin resistance and glucose intolerance (Fluoride Alert Network, 2015). The main sources of fluorine are fluoridated water, fluoridated supplements, fluoridated dentifrices and processed baby foods consumed before the age of six years (Mascarenhas, 2000).

Baby foods are food products designed to provide for the nutritional needs of infants. Baby food samples usually have complex matrices including proteins, oils, minerals, carbohydrates and minor ingredients (Ozbek & Akman, 2012c). There are many studies for determining fluoride in baby food samples. In Japan, fluoride contents of various baby foods were determined using fluoride ion selective electrode after a long, laborious and complicated sample preparation procedure applying microdiffusion at 60 °C for 12 h prior to analysis. The fluoride concentrations in powdered milk

and various types of infant foods (gruels, meat and fish, vegetable, fruit group) were found in the range of 0.30 to 1.00 and 0.02–2.91  $\mu\text{g g}^{-1}$  (Tomori, Koga, Maki, & Takaesu, 2004). The fluoride concentrations in the typical Brazilian meal (rice with beans) and in processed infant foods were determined using ion selective electrode after separating the fluoride applying microdiffusion technique for 12–18 h and subsequently a series of complicated procedures. The fluoride concentrations were found as 0.12 to 1.63  $\mu\text{g g}^{-1}$  in porridges, 0.07 to 0.37  $\mu\text{g g}^{-1}$  in powdered milk, 0.84 to 3.84 in  $\mu\text{g g}^{-1}$  soybean formula, 0.84 to 1.67  $\mu\text{g g}^{-1}$  in milk-based formula, and 0.04 to 0.54  $\mu\text{g g}^{-1}$  in other foods (Casarin, Fernandes, Lima-Arsati, & Cury, 2007). USDA reported the mean fluoride concentrations of all kind of baby foods and biscuits between 0.01 and 0.70  $\mu\text{g g}^{-1}$  (U.S. Department of Agriculture, 2005). In all those studies, concentrations of free fluoride ion rather than total fluorine were determined.

Fluorine has been determined by various methods such as ion selective electrodes (ISE), ion chromatography (IC) and UV–vis etc. Nevertheless, each of them has its own limitations and disadvantages such as high cost, time consumption, poor precision, selectivity and moreover none of them is free of interferences. Practically, fluorine cannot be determined by conventional atomic absorption spectrometry (AAS) using a hollow cathode lamp (HCL) because its atomic resonance absorption line is below 180 nm, in vacuum UV region and far beyond the working range of the instrument. Fluoride was determined indirectly after precipitated with

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silver, calcium etc., and then dissolving of the precipitate and measurement of the metal by AAS. Alternatively, fluorine was determined by the formation of a diatomic molecule between fluorine and a molecule forming element and then measurement of the molecular absorption at one of its finely structured rotational lines using  $D_2$  or an appropriate hollow cathode lamp (HCL) having an appropriate emission line (Tsunoda, Haraguchi, & Fuwa, 1980).

High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) is quite a new and challenging instrument which provides a resolution ( $\lambda/\Delta\lambda$ ) of 175,000 in a 0.3–1 nm range, corresponding to a bandwidth of 1.6 pm per pixel at 200 nm, to 6.4 pm at 800 nm (Welz et al., 2010). Therefore, it is possible to select a very narrow wavelength (a few pico meters) overlapping exactly with analytical line of the molecule by seeing its spectral neighboring environment and to take measure of spectral interferences. By utilizing the capabilities of HR CS-AAS, a number of studies have been carried out for the determination of fluorine in various samples using a hyperfine rotational line selected from the structural spectrum of an analyte-containing molecule. For this purpose, molecular absorption of CaF, GaF, AlF, BaF and SrF were successfully used (Gleisner, Einax, Mores, Welz, & Carasek, 2011; Gleisner, Welz, & Einax, 2010; Mores, Monteiro, Santos, Carasek, & Welz, 2011; Ozbek & Akman, 2012a,b, 2013a,c, 2014, 2015). Welz et al. (2009) reviewed determination of sulphur, phosphorus and the halogens using line source conventional flame and graphite furnace AAS and HR CS-AAS.

In conventional AAS studies, samples are digested mostly by mineral acids and applying heat which is causes one of the most important sources of error. There are many drawbacks of sample digestion i.e. (i) contamination or loss of the analyte, (ii) health and corrosion risks due to gases vaporization of solvent, (iii) increased the environmental pollution caused by solvents, (iv) need of expensive microwave assisted digestion systems and its consumables (v) required time and chemicals. In order to overcome these drawbacks, samples are introduced to the graphite furnace of AAS directly in solid forms. However, solid sampling has some disadvantages such as high background absorption, calibration difficulties, lack of sample introduction facility (or need of a specific device), low precision due to sample inhomogeneity in microscale, etc. If the above-mentioned problems are eliminated and the experimental conditions for solid sampling are optimized to obtain accurate results, the solid sampling technique becomes more appropriate and attractive compared to digestion (Baysal & Akman, 2010; Baysal & Akman, 2011a,b; Baysal, Ozbek, & Akman, 2010, 2011; Kelestemur & Özcan, 2015). Fluorine has also been determined in some samples directly by solid sampling HR-CS GFAAS (SS-HR-CS GFAAS) too, by MAS of various diatomic molecules i.e. CaF and AlF (Borges et al., 2016; Borges, Franco, Welz, Carasek, & Vale, 2014; Flores, Barin, Flores, & Dressler, 2007; Machado et al., 2015).

The aim of this study was to develop a method for the determination of total fluorine in baby foods via molecular absorption CaF generated in a graphite furnace using a solid sampling high resolution continuum source graphite furnace molecule absorption spectrometry (SS-HR-CS GF MAS).

## 2. Experimental

### 2.1. Instrumentation and reagents

All measurements were carried out using a ContrAA 700 Analytik Jena (Germany) High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometer (HR-CS GF AAS), equipped with SSA600 solid sampler and a 300 W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany). Argon (99.99%) was

used as a purge gas. The molecular absorbance for CaF was measured at 606.440 nm. The absorbance's were given as the summation of three pixels, i.e. central pixel  $\pm 1$  (CP  $\pm 1$ ). The graphite furnace program used for the determination of fluorine is given in Table 1. All chemicals were of analytical reagent grade (Merck, Germany). Stock solution ( $1000 \text{ mg L}^{-1}$ ) of fluorine was prepared from NaF further diluted with ultrapure water daily whereas calcium (molecule forming element) was prepared from  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ . The bush branches certified reference material (NCS DC 73349) which has  $23 \pm 4 \mu\text{g g}^{-1}$  of fluorine was obtained from National Analysis Center for Iron & Steel (NACIS), Beijing, China.

### 2.2. Procedure

Baby foods were directly used after dried at  $100^\circ\text{C}$ . The samples were put on the platforms of the solid autosampler between 0.5 and 1.2 mg, weighed automatically in the balance of the autosampler with 0.001 mg of precision,  $10 \mu\text{L}$  of  $4000 \mu\text{g mL}^{-1}$  of calcium was then injected on the sample and transferred into the furnace. All solutions were injected as  $10 \mu\text{L}$  by means of built-in liquid dispenser of the autosampler.

## 3. Results and discussion

### 3.1. Choice of molecule forming metal and wavelength

As mentioned previously, fluorine cannot be determined directly by conventional atomic absorption spectrometry since the primary resonance atomic absorption wavelength of fluorine is at 95 nm which is in far beyond vacuum UV. The method described in this study is based on the formation of a diatomic molecule of fluorine with a metal in the gas-phase of a graphite tube and measurement its molecule absorption at one of its finely structural rotational lines. The diatomic molecule should be stable enough to remain stable in volatilization (molecule formation) step. Diatomic molecules with bond dissociation energies higher than  $500 \text{ kJ mol}^{-1}$  are the most suitable for this purpose. In addition, the sensitivity of the diatomic molecule should be high enough to detect the low fluorine concentrations in the samples. Finally, since the molecule forming element is used at quite high concentrations, it should not be harmful for human life and environment. The bond dissociation energy of CaF is around  $550 \text{ kJ mol}^{-1}$ . In previous studies, calcium was successfully used for the determination of fluorine via CaF (Borges et al., 2014; Huang et al., 2014; Ozbek & Akman, 2013a, 2015). Therefore, calcium was selected as a suitable molecule forming element to form CaF for the determination of total fluorine.

Ideally, to detect the low analyte concentrations in the sample, the most sensitive rotational molecular absorption line of the diatomic molecule is used. In addition, the molecular absorption line selected for analysis should not overlap with any atomic absorption and one of the structured lines of molecular band of matrix concomitants. CaF has an absorption band which consisted of a

**Table 1**

The optimized graphite furnace temperature-time program for the determination of fluorine via CaF with solid sampling.

| Step                                   | Temperature ( $^\circ\text{C}$ ) | Ramp ( $^\circ\text{C s}^{-1}$ ) | Hold time (s) | Gas flow, ( $\text{L min}^{-1}$ ) |
|--|----------------------------------|----------------------------------|---------------|-----------------------------------|
| 1. Drying                              | 110                              | 5                                | 10            | 2.0                               |
| 2. Pyrolysis                           | 1000                             | 300                              | 10            | 2.0                               |
| 3. Gas adaption                        | 1000                             | 0                                | 5             | Stop                              |
| 4. Molecule formation (Volatilization) | 2200                             | 2000                             | 5             | Stop                              |
| 5. Cleaning                            | 2700                             | 500                              | 4             | 2.0                               |

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