

Direct determination of fluorine in milk powder by molecular absorption spectrometry using electrothermal graphite furnace

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Abstract

The direct determination of fluorine in milk via the molecular absorption of calcium mono-fluoride (CaF) was performed using HR-CS MAS.

Introduction

Fluorine is an essential trace element for human health, but the intake of high amounts may negatively affect bones and teeth. To overcome these problems, fluorine therapy methods are widely used, as fluoridation of toothpaste, drinking water, salt and milk. On the other hand, exposure to fluorine in excessive amounts can interfere on bone formation and can cause dental and/or skeletal fluorosis. Therefore, the concentration of fluorine needs to be controlled and personal fluorine ingestion should be kept between 2 and 3 mg day⁻¹. Fluorine is usually determined using potentiometry with fluoride ion-selective electrodes or ion chromatography. However, for both analytical techniques requires a previous sample preparation step to convert the sample matrix to a suitable solution. Nevertheless, these methods are commonly time consuming and prone to analyte losses or contamination. The recent development of commercial equipment for high-resolution continuum source atomic absorption spectrometry (HR-CS AAS), which is equally applicable for the measurement of molecular absorption spectrometry (MAS) allowed the determination of fluorine using molecular absorption in flame or graphite furnace. In this work, a CaF molecular absorption band at 606.440 nm was chosen for fluorine determination in milk powder using direct solid sampling and graphite furnace. It is important to emphasize that it is the first time that direct solid sample is used for F determination using HR-CS MAS.

Results and discussion

Graphite furnace mode 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), a high resolution double monochromator consisting of a prism, an echelle monochromator and a charge-coupled device (CCD) array detector was used for all measurements. Determination of fluorine was performed via the rotational molecular

absorption line of CaF at 606.440 nm by HR-CS-MAS by direct solid sampling. Parameters, such as the graphite furnace temperature program and the concentration of chemical modifier were investigated. For the proposed HR-CS MAS method, 10 µL of standard solutions or 1 mg of milk powder plus 10 µL of 4 g L⁻¹ of calcium diluted from stock calcium nitrate solution (used as modifier and for molecule formation) were weight and/or pipetted into the graphite tube. To cover the graphite tube and platform with zirconium, 20 µL of a 1 g L⁻¹ Zr solution (as nitrate) was pipetted, dried and then thermally treated at 1100 °C for 10 s. The procedure was repeated 10 times. Optimized temperatures for pyrolysis and vaporization were 700 and 2100 °C, respectively. Accuracy of the proposed method was evaluated by comparison of results with those obtained by microwave-induced combustion (MIC) digestion and further determination by ISE using a spiked milk powder sample containing 10 µg g⁻¹ of F. Concentration of F in spiked milk powder sample was 10.6 ± 0.2 µg g⁻¹ (determination by HR-CS MAS). Moreover, the limit of detection, limit of quantification, characteristic mass and linear range were evaluated being 0.72 ng, 2.4 ng, 50.6 pg and 50 ng, respectively.

Conclusions

It was demonstrated that F can be determined by HR-CS MAS with good precision, sensitivity and accuracy. In addition, the feasibility for the direct analysis of solid samples was demonstrated, which practically does not require sample preparation, minimizing the risk of analyte losses and contamination. Additionally, aqueous solutions may be used for calibration, which is an advantage as no solid reference materials are required. The procedure was simple and fast and the LOD was considered suitable for determination of F in milk powder.

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