Straightforward silicon determination in water-in-oil-in-water emulsions used for silicon supplementations in food by high-resolution continuum source flame atomic absorption spectrometry ☆

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ABSTRACT

Water-in-oil-in-water ($W_1/O/W_2$) double emulsions are complex liquid dispersions employed to entrap, protect and control the release of different substances such as minerals in cosmetics, pharmaceuticals, and food. The present paper proposes a simple and fast analytical procedure for silicon determination in double emulsion samples formulated for the supplementation of silicon in different food products. Silicon determination was performed by flame atomic absorption spectrometry (FAAS) at the main analytical line (251.611 nm) using a high-resolution continuum source instrument. The introduction of the sample in the spectrometer in a continuous or discontinuous mode and the influence of double emulsion matrix on silicon absorbance signals were investigated. At the optimized conditions, the double emulsion samples were analysed using silicon standards in ultrapure water for calibration. The limits of detection (LODs) were 0.04 and 0.11 mg L^{-1} and the upper limits of silicon linear working ranges were up to 23 and 70 mg L^{-1} for continuous and discontinuous sample introduction modes, respectively. Silicon spiked double emulsion samples were analysed for validation purposes. The good recoveries (within 95–105%) demonstrated the suitability of the proposed method.

1. Introduction

Water-in-oil-in-water ($W_1/O/W_2$) emulsions are complex multiphase liquid systems in which aqueous droplets are dispersed in larger oil drops that are in turn dispersed within a second aqueous continuous phase. In this way, these compartmentalized systems permit to encapsulate, protect and deliver at a controlled rate water-soluble chemical substances such as drugs, vitamins, active components, nutrients, or minerals initially entrapped in the internal aqueous phase. Due to these characteristics, double emulsions are employed in cosmetics, pharmaceutical and food industries to incorporate these substances and improve the properties of their products [1–6].

Silicon is an element widely used for diverse industrial applications including its use as additive in food and beverages. Silicon is not considered nowadays as an essential element for humans because its exact biochemical function is still unclear. However, it is suspected that this metalloid plays a key role in the development of bones, cartilages, and other connective tissues and its deficiency could produce aging of hair,

nails, and skin. In addition, recent findings indicate that silicon may have a modulating effect on the immune and inflammatory response, and it has been associated with mental health. Due to the benefits of this element, silicon supplementations in food, cosmetics, and pharmaceuticals have drawn an increasing interest in the last decade [7–11]. In this regard, double emulsions can be an adequate option to encapsulate bioavailable and water-soluble silicon forms and develop silicon delivery systems. For example, different $W_1/O/W_2$ emulsions have recently been investigated to evaluate their possible use as potential ingredients for the development of healthier foods [3]. To study the encapsulation processes and ensure the quality criteria of new products that incorporate silicon in these double emulsions, adequate analytical methods for accurate and precise silicon determination are required.

Silicon determination is considered an important challenging task, mainly when samples with complex organic matrices such as oils, pharmaceutical formulations, or food products must be analysed. Analytical methodologies based on atomic techniques, neutron

activation analysis, nuclear magnetic resonance, and X-ray fluorescence have been applied for silicon determination in this kind of samples. [7, 12]. Among them, atomic spectrometry techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), ICP optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS) with flame or graphite furnace atomizers are the most commonly employed to carry out the analysis after an adequate pre-treatment of the samples [12, 13]. In these atomic spectrometry techniques, the analytical response of silicon is highly dependent on the chemical form of the analyte and the nature of the sample [12, 14, 15].

The determination of metals and metalloids in organic matrices by ICP-MS or ICP-OES can mainly be affected by changes on the plasma characteristics, the formation of carbon deposits and the appearance of spectral interferences [16, 17]. In fact, methods based on ICP-MS are highly affected by spectral interferences due to polyatomic ions produced by the presence of oxygen, carbon and nitrogen (e.g. $^{12}C^{16}O^{+}$, $^{14}N_2^{+}$, $^{14}N^{16}O^{+}$) that can influence the accurate determination of silicon isotopes [18]. Although methods based on AAS with flame or graphite furnace atomizers usually present a higher tolerance to organic matrices, they also show disadvantages in silicon determination, some of them similar to those observed using ICP-MS or ICP-OES methods. For example, an important limitation for the silicon determination in AAS using graphite furnace atomization (GFAAS) is the formation of volatile compounds such as SiO and/or refractory silicon carbides (SiC) so adequate modifiers are required to avoid an inaccurate determination [19–22]. Additional difficulties can be found using conventional line-source AAS instruments due to radiation scattering effects, that are more frequent at the short wavelengths of the silicon resonance lines (251.611/251.432 nm), as well as by spectral interferences [23]. In flame atomic absorption spectrometry (FAAS), the formation and occurrence of diatomic molecules with rotational fine structure such as PO, CS, or NO, and their molecular spectra are due to the atomizer (the flame composition) and the matrix constituents of the sample or standard introduced in the spectrometer [20, 24]. For the silicon determination, a spectral interference due to the CS molecule formed in the flame has been observed in the analysis of samples containing S compounds. The presence of vanadium, cobalt, iron, and/or tungsten at high concentrations can cause spectral interferences since some low sensitivity absorption lines of these elements are located close to the silicon lines at 251.611 nm and 251.432 nm [25]. Moreover, the absorbance signal registered for silicon determination using a conventional line-source AAS spectrometer is typically a combined signal from the silicon lines at 251.611 nm and 251.432 nm [20]. Using a high-resolution continuum source FAAS (HR-CS FAAS) spectrometer, these drawbacks can be minimized or eliminated. The excellent resolution provided by this spectrometer permitted to use the silicon absorbance signal at 251.611 nm separated from the silicon signal at 251.432 nm, and ensure the absence of spectral interferences due to the presence of high amounts of other elements such as vanadium or iron [25]. In addition, the spectral interference due to CS molecule was effectively corrected by the least-squares background correction procedure available in the software of this instrument [25, 26].

Regardless of the atomic spectrometry technique used for silicon determination, previous treatments of the sample for total matrix decomposition and minimization of spectral interferences are usually required. These sample treatments present important drawbacks derived from the possible loss of the analyte in highly volatile forms and the risk of contamination due to the ubiquity of this element [7, 12]. Indeed, in an interlaboratory study carried out about silicon determination in biological matrices by spectrometric techniques the main problems arose when the sample digestion pre-treatments were needed prior to the analysis [13]. Due to these problems, methods based on direct analysis of the sample are attractive approaches for silicon determination. Direct solid sampling has been employed for silicon determination by GFAAS in polyamide [22], hardly soluble oxides [27], or plant materials [28]. Because methods based on FAAS are simple, widely used and relatively low cost, the possibility of carrying out the analysis without a previous sample digestion or only with a very simple sample treatment is a very interesting issue. Analytical methodologies based on FAAS have been used and reported for the quantification of silicon. For instance, we have developed a straightforward sequential method based on HR-CS FAAS for the determination of copper, zinc, manganese, magnesium and silicon in beverages, herbal infusions and dietary supplements [29]. Different approaches to minimize the sample treatment have been proposed for silicon determination in oily samples. Oliveira et al. [30] reported the direct determination of silicon in vegetable oils and biodiesel samples by HR-CS FAAS after the dilution with xylene and using standards prepared in xylene for calibration. As an alternative to the sample dilution in organic solvents, the preparation of oil-in-water emulsions has been successfully used as sample pre-treatment to determine magnesium, chromium, copper, lead, nickel, aluminium and silicon in lubricating oils by FAAS [31]. In general, the main advantages attributed to the use of emulsified systems as a sample preparation procedure in analytical chemistry are that they do not require the previous destruction of the sample matrix or the use of large amounts of organic solvents as diluents [32, 33]. Compared to the other sample pre-treatments, the sample handling and the reagent addition are minimized in the preparation of emulsions, decreasing the risk of sample contamination. Moreover, an emulsified system with an adequate stability and a similar viscosity to the observed for aqueous solutions can be achieved optimizing the preparation procedure. These are very important characteristics to analyse samples with complex organic matrices by spectrometric methods since the calibration can be performed using aqueous standards. Although, emulsified systems have been successfully applied to sample preparation of petroleum-based products, foodstuffs and cosmetics for metal determination by atomic spectrometry techniques [32, 33] few works have been devoted to silicon determination [21, 31, 34].

Taking into account the applicability of silicon encapsulation in $W_1/O/W_2$ emulsions and the problems for silicon determination in complex matrices, the aim of this work is to optimize a simple and fast FAAS methodology for the determination of silicon in $W_1/O/W_2$ emulsions formulated as potential ingredients to obtain healthier food products. In a previous paper [3], we studied the physicochemical properties and the encapsulation of silicon in these double emulsions. In that work, the silicon encapsulation efficiency in the different prepared double emulsions was evaluated in an indirect mode by measuring the released silicon concentration in the outer aqueous phase. For this purpose, after the preparation of the double emulsions, they were centrifuged to separate the fat globules from the outer aqueous phase. The encapsulation efficiency was estimated from the initial silicon amount added to the inner aqueous phase and the silicon content determined in the outer aqueous phase. In this work, our objective is to design a FAAS method for silicon determination in these double emulsion samples directly or with a minimal sample treatment. To achieve this purpose, the measurement parameters and sample introduction conditions were optimized. In addition, the influence of the double emulsion matrix on the absorbance signals of silicon was investigated. The feasibility to perform the calibration with standards prepared in ultrapure water was evaluated and the principal analytical parameters were calculated. A HR-CS FAAS instrument was employed in this work because the remarkable instrumental and signal processing software advantages of this equipment permit to get excellent analytical performances for silicon determination in complex samples.

2. Experimental

2.1. Instrumentation and measurement conditions

A contrAA 700 model high-resolution continuum source atomic absorption spectrometer (Analytik Jena, Germany) with a flame atomizer system was used for silicon measurements. This instrument