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Multivariate optimization of ultrasound-assisted extraction using Doehlert matrix for simultaneous determination of Fe and Ni in vegetable oils by high-resolution continuum source graphite furnace atomic absorption spectrometry

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ABSTRACT

A method for simultaneous determination of Fe (232.036 nm) and Ni (232.195 nm) in vegetable oil samples by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) after an acid extraction of the analytes is proposed. In the extraction step, hydrochloric, nitric and acetic acid solutions were tested. The optimization of the procedure was performed by applying Doehlert matrix, and multiple response was used for simultaneous evaluation of the performance of the extraction. The optimum conditions were: extraction time of 17 min, extraction temperature of 39 °C and sonication amplitude of 42%, employing 0.5 mol L^{-1} HCl as the extracting solvent. The limits of quantification were 60 and 160 ng g^{-1} for Fe and Ni, respectively. The method was applied to the analysis of vegetable oil samples and the results were compared with a method employing inductively coupled plasma optical emission spectrometry (ICP OES).

1. Introduction

Vegetable oils are very important for the food industry and for the production of fatty acids, glycerin, oils and biodiesel (Brito et al., 2012; Lepri et al., 2011). Most of the vegetable oil produced is destined for the human consumer (Trindade, Dantas, Lima, Ferreira, & Teixeira, 2015). They are associated with the production of satiety signals that regulate meal size, and their controlled and regular ingestion may be associated with the prevention of stress, cardiovascular and brain problems (Lepri et al., 2011; Denis, Potier, Vancassel, Heberden, & Lavialle, 2013). The determination of metal contaminants is crucial for evaluation of the quality (Tokay & Bagdat, 2015). These contaminants may come from the soil, from fertilizer or from roads and/or industries near plantations. Furthermore, the contaminants may also be introduced during oil production, transportation and storage (Llorent-Martínez, Fernández-de Córdova, Ortega-Barrales, & Ruiz-Medina, 2014). The presence of metals such as Fe and Ni, even at low concentrations, may catalyze and increase the oxidation process of these matrices, changing their characteristic properties (Baran & Yasar, 2010). Such changes affect the characteristics of the samples and reduce the life cycle of these products.

Atomic spectrometric techniques have been used for the determination of metals and metalloids in different matrices at different concentration levels, including biodiesel, bioethanol, automotive fuels and vegetable oil samples (Lepri et al., 2011). Due to the complexity of the matrices, the determinations involve a pretreatment step to adequately prepare the sample for the metal determination. As preparation steps, procedures such as liquid-liquid extraction (Tokay & Bagdat, 2015; Trindade et al., 2015), solid phase extraction (Asci, Efendioglu, & Bati, 2008), ashing (Garrido, Frias, Diaz, & Hardisson, 1994), dilution with organic solvents (Bozhanov & Karadjova, 2008), emulsion or microemulsion formation (Benzo et al., 2006; Nunes et al., 2011) and acid digestion (Llorent-Martínez et al., 2014) are often applied before the determination by an atomic spectrometric technique.

High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) can be used for determination of metals in vegetable oil samples with advantages compared to line source atomic absorption spectrometry (LS AAS). One of the advantages is the possibility of the simultaneous determination of two or more elements. This possibility depends on some specific factors: (i) the

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elements must have absorption lines within the spectral interval accessible to the coupled charge device (CCD) detector; and (ii) a thermal condition of compromise for the analytes must be established, so that the pyrolysis and atomization temperatures are optimized according to the volatility of each of the elements to be determined simultaneously; in addition, (iii) the choice of a chemical modifier must provide acceptable thermal conditions for both analytes (Resano, Flórez, & García-Ruiz, 2013). An inherent consequence of the need to choose the spectral lines in the same spectral window is that one or more lines used will not necessarily be the most sensitive for a particular element. Therefore, the selection of absorption lines is not an easy task for simultaneous determination because the use of lines less sensitive can fail to be compatible with the concentrations of the analytes in samples. Thus, the use of strategies to increase the sensitivity of the method for the simultaneous determination of multiple analytes is frequently required (Dos Santos et al., 2009; Vignola, Borges, Curtius, Welz, & Becker-Ross, 2010), combining the most sensitive atomic lines or employing a preconcentration step, for example.

High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) has been used for the simultaneous determination of elements in different matrices such as, for example, Fe and Ni in biological samples (Gómez-Nieto, Gismera, Sevilla, & Procopio, 2013), Cr and Fe in crude oil (Dittert et al., 2009), and Cd and Fe in beans and soils (Dos Santos et al., 2009). High-resolution continuum source flame atomic absorption spectrometry (HR-CS F AAS) was used in the sequential determination of metals, including Fe and Ni, in vegetable oils (Trindade et al., 2015), and more recently HR-CS GF AAS and direct solid sample analysis was employed for the simultaneous determination of Fe and Ni in vegetables (Pozzatti, Nakadi, Vale, & Welz, 2017). However, analytical strategies for simultaneous determination of Fe and Ni in vegetable oil samples by HR-CS GF AAS in association with ultrasound-assisted extraction have not been found in the literature.

Multielement determination by HR-CS GF AAS is not easily implemented when compared with HR-CS F AAS (Resano, Rello, Flórez, & Belarra, 2011). Despite this limitation, HR-CS GF AAS has been employed as result of its good sensitivity and tolerance to complex matrices, including sequential and simultaneous multielement determinations (Almeida, Souza, & Teixeira, 2018). In addition, the use of smaller amounts of reagents during sample preparation, lower limits of detection and the combination of secondary absorption lines for application in the simultaneous determination of two or more analytes are advantages of HR-CS GF AAS in comparison to HR-CS F AAS. Thus, the present work proposes a method for the simultaneous determination of iron and nickel in vegetable oil samples by HR-CS GF AAS after an ultrasound-assisted acid extraction procedure.

2. Experimental

2.1. Instrumentation

The determinations were performed using a model ContrAA 700 high-resolution continuum source graphite furnace atomic absorption spectrometer from Analytik Jena AG (Jena, Germany). The spectrometer is equipped with a XBO301 xenon short-arc lamp (GLE, Berlin, Germany) as a continuum radiation source, a charge-coupled device (CCD) array detector and a double-echelle monochromator. All experiments were carried out using pyrolytically coated graphite tubes with an integrated PIN platform and transversal heating. An MPE 60 furnace autosampler (Analytik Jena) was used for introduction of liquid solutions. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas with a flow rate of 2.0 L min^{-1} during all stages, except during atomization, when the flow was stopped. The absorbance signal was measured by the integrated peak area using 3 pixels for both metals. The Table 1 shows the graphite furnace temperature program used for the simultaneous determination of Fe and Ni. For this purpose, secondary atomic lines at 232.036 and 232.195 nm were used for iron and nickel determination, respectively, after optimization of the factors extraction time, temperature and sonication amplitude of the extraction step via a multiple response function.

Table 1
Graphite furnace temperature program used for the simultaneous determination of Fe and Ni in vegetable oil samples by HR-CS GF AAS.

Stage	Temperature, °C	Ramp, °C s^{-1}	Hold time, s	Gas flow rate, L min^{-1}
Drying 1	100	3	20	2.0
Drying 2	150	5	10	2.0
Pyrolysis 1	350	50	20	2.0
Pyrolysis 2	1200	300	10	2.0
Auto-zero	800	0	5	0.0
Atomization	2600	FP	4	0.0
Cleaning	2650	500	4	2.0

FP: Full power.

A Varian Vista (Mulgrave, Australia) inductively coupled plasma optical emission spectrometer was used for comparison purposes. The spectrometer was equipped with a Sturman–Master chamber, a V-Groove nebulizer and a charge coupled device (CCD) detector with operational conditions for the monitoring of elements at wavelengths between 167 and 785 nm. The measurements were performed under the manufacturer's recommended conditions with a power level of 1.3 kW and plasma, auxiliary and nebulizer gas flow rates at 15.0 L min^{-1}, 1.5 L min^{-1}, and 0.7 L min^{-1}, respectively. For the analysis, a pre-alignment of the torch was performed with a solution of 5.0 mg L^{-1} Mn, and the calibration of the equipment was performed with a multi-element reference solution.

For the acid extraction of Ni and Fe from vegetable oil samples, a model 75D ultrasonic bath from VWR International™ (Cortland, New York), with 60 kHz power, 2-L internal capacity and a controlled and adjustable temperature was used. The extractions were performed in conical centrifuge tubes with 15 mL internal capacity. All weighings were performed using a model TE214 S analytical balance from Sartorius (Goettingen, Germany), with accuracy of ± 0.1 mg. A tube-type vortex stirrer (Phoenix AP 56, Araraquara, Brazil) was used for mixing.

2.2. Reagents, solutions and samples

Deionized water with a specific resistivity of 18 MΩ cm from a Milli-Q water purification system (Millipore, Bedford, USA) was used for the preparation of the samples and standards. All containers and glassware had previously been decontaminated in 1.4 mol L^{-1} nitric acid for at least 24 h and rinsed three times with deionized water before use.

To evaluate the best extraction solvent, hydrochloric acid (Qhemis, Hexis Scientific, Brazil), nitric (Merck, Darmstadt, Germany) and acetic acid (Qhemis, Scientific Hexis, Brazil) were prepared from dilutions of their concentrated solutions with water. Aqueous standard solutions of iron and nickel were prepared by diluting stock standards containing 1000 µg g^{-1} of the metal (Qhemis) in 0.5 mol L^{-1} HCl. The working organic solutions were prepared by weighing and diluting of a metal multi-element standard (AccuStandard, Inc., New Haven, USA, Catalog Number WM-21-90X) containing 900 µg g^{-1} of Fe and Ni in hydrocarbon oil to the desired concentrations. The analytical blanks were prepared using the base mineral oil (AccuStandard, Inc., New Haven, USA) free of the metals analyzed. Calibration curves were obtained over the concentration ranges from 0.06 to 1.75 µg g^{-1} and from 0.16 to 1.75 µg g^{-1} for Fe and Ni, respectively. A solution of Mg 0.1% (w/v) was prepared by diluting $Mg(NO_3)_2$ (Merck) with water.

The vegetable oil samples of cotton, sunflower, canola, soybean and corn oils were purchased at a local supermarket in the city of Salvador, Bahia, Brazil. These samples were stored protected from light at room temperature before the analysis.