Original research article

The use of diluted formic acid in sample preparation for macro- and microelements determination in foodstuff samples using ICP OES

Aline Fernandes de Oliveira[a,b], Caroline Santos da Silva[a,b,*], Silmara Rossana Bianchi[c], Ana Rita Araujo Nogueira[b]

[a] Group for Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, Rd. Washington Luiz, km 235, Caixa Postal 676, 13565-905, São Carlos - SP, Brazil
[b] Embrapa Pecuária Sudeste, Rd. Washington Luiz, km 234, Caixa Postal 339, 13560-970, São Carlos - SP, Brazil
[c] Embrapa Solos, Rua Jardim Botânico, 1024, 22460-000, Rio de Janeiro - RJ, Brazil

ARTICLE INFO

ABSTRACT

A fast analytical method for determination of macro- and microelements in foodstuff samples by ICP OES using diluted organic acid extraction was developed. The sample preparation was carried out employing ultrapure 50% (v/v) formic acid on a heating block. The elements studied were Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn. The accuracy of the method was evaluated by analyzing three different certified reference materials (NIST (1577b) bovine liver, NIST (1515) apple leaves and NIST (8435) whole milk powder), and the recovery percentages ranged from 80.7 to 114%. The results obtained showed good agreement at a confidence level of 95% with the certified values, presenting RSD values < 20%. The limits of detection ranged from 0.056 mg/kg to 0.06 g/100 g. This solution-based method demonstrated the feasibility of using diluted organic acid, presenting high sample throughput and was considered simple and adequate for determining these analytes in foodstuff samples in routine analysis.

1. Introduction

The ideal sample preparation procedure should be effective, reproducible, fast, safe and environment-friendly (Krug, 2010; Rocha et al., 2013). The determination of macro- and microelements generally implies a digestion step using cavity microwave ovens employing inorganic acids with high oxidant power, under high pressure and temperature (Arruda, 2007). Although studies have shown the efficiency of diluted inorganic acid for digestion of different samples, the use of diluted organic acids for sample preparation is not conventional (Araújo et al., 2002; Trevizan et al., 2007; Santos et al., 2013; Barbosa et al., 2015). In general, sample preparation is one of the most important steps to measure trace elements and methods involving digestion with oxidant acids and heating are often employed. The conventional sample preparation procedure is considered time-consuming, requires large amounts of corrosive and toxic reagents, which raises the cost of

analysis and is also susceptible to contamination and/or losses of the analyte by volatilization. Formic acid has been used as an alternative reagent for the solubilization of different matrices, mainly due to its availability, simplicity and safety (Silva et al., 2012; Tormen et al., 2010). Moreover, the use of diluted organic acids has the advantage of reducing the amount of reagent, thus minimizing cost and reagent waste, extending the lifetime of instruments, and lowering the blank signals, consequently obtaining lower limits of quantification (LOQs) (Gonzalez et al., 2009).

Formic acid has also been widely employed in extraction procedures for speciation analysis (Vieira et al., 2007). Some articles have reported the use of concentrated formic acid for biological samples solubilization for determination of many elements (Tormen et al., 2010, 2012; Lopes et al., 2016). The main use of formic acid is in elemental extraction for speciation analysis, targeting the use of non-oxidant acids (Raab et al., 2005; Batista et al., 2014; Narukawa et al., 2014; Aborode et al., 2015).

Scriver et al. (2005) proposed the solubilization of biological samples from marine origin using formic acid combined with vortex, heating and ultrasound bath for determination of Ag, As, Cd, Cu, Cr, Fe, Ni, and Se by electrothermal atomic absorption spectrometry (ET-AAS) and Na, Ca, K, Mg, Fe, Cu and Mn by inductively coupled plasma optical emission spectrometry (ICP OES). Tormen et al. (2012) proposed the use of concentrated formic acid for sample preparation to determine As, Ba, Cd, Co, Cu, Fe, Ga, Mn, Mo, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn in biological samples by inductively coupled plasma mass spectrometry (ICP-MS). The authors also used the same decomposition process for determination of As, Se and transition metals by electrothermal vaporization combined with inductively coupled plasma mass spectrometry (ETV-ICP-MS) in biological samples. In another study, Lopes et al. (2016) employed formic acid to extract and determine trace elements such as Al, As, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, V and Zn in shelled Brazil nut and babassu coconut samples by ICP-MS. Whole nut, oil and solid residue (cake) were analyzed. Microwave-assisted nitric acid digestion was used as a comparative method to the proposed extraction (Lopes et al., 2016).

Wet microwave-assisted digestion is still considered the state-of-the-art of sample preparation, but many routine laboratories do not have this instrumentation due to the price and maintenance cost of instruments and accessories compared to heating blocks (Flores, 2014). Besides low cost, heating blocks are more common in laboratories because they are easy to install and use and require few or no accessories.

Based on the mentioned studies, the present work evaluated the use of diluted organic acid for sample preparation as an alternative to the conventional methods targeting macro- and microelements, due to their relationship with the healthy growth of plants and animals. Looking forward to the development of an alternative sample preparation procedure employing diluted organic acid for determination of macro- and microelements in different foodstuff samples, we also evaluated the efficiency of the extraction.

2. Material and methods

2.1. Instrumentation

All analytical weighing was performed using an APX-200 balance (Denver Instrument GmbH, Gottingen, Nie-dersachsen, Germany). The sample decomposition was realized in a heating block digester (Tecnal, Piracicaba, SP, Brazil) with closed perfluoroalkoxy (PFA) vessels (Savillex, Eden Prairie, MN, USA). A centrifuge was used to separate the supernatant and solid residue (Z 200 A, Hermle Labortechnik, Wehingen, Germany). The acid digestion was performed using a microwave cavity oven (Multiwave 3000 microwave sample preparation system, Anton Paar, Graz, Austria) equipped with 16 fluoropolymer vessels and polyether ether ketone (PEEK) jackets. The nitric and formic acid used in the comparative sample preparation procedures were subdistilled using a SubPur apparatus (Milestone, Sorisole, Italy). All analytical measurements were performed in an ICP OES (iCAP 6000 Series Duo, Thermo Scientific; Cambridge, UK) with axial and radial view, equipped with simultaneous CID detector and Echelle grating, peristaltic pump, concentric nebulizer, cyclonic spray chamber, and demountable quartz plasma torch with central tube injector having a 2.0 mm internal diameter. The instrumental parameters used for the analytical measurements were: 1150 W RF power; 12.0 L/min plasma gas flow rate; 0.5 L/min auxiliary gas flow rate; 0.5 L/min nebulizer gas flow rate; 1.0 L/min. Three wavelengths (nm) of each element were monitored, but only the best ones based on the accuracy using formic acid are reported, among them atomic (I) or ionic (II) lines: 396.8 (II) and 422.6 (I) for Ca; 324.7 (I) for Cu; 239.5 (II) for Fe; 769.8 (I) for K; 279.5 (II) for Mg; 259.3 (II) and 260.5 (II) for Mn; 589.5 (I) for Na; 214.9 (I) for P; 213.8 (I) and 202.5 (II) for Zn, in dual-view reading, axial (A) and radial (B). All results (three wavelengths) for each CRM were compared between nitric and formic acid methods, and in the case

of multiple lines, the same one was prioritized. When this was not possible the line providing the best accuracy was used for each foodstuff sample.

2.2. Samples, reagents and solutions

All glassware was kept in a 10% (v/v) HNO_3 solution for 24 h and rinsed with deionized water from a purification system (Millipore, Bedford, USA). Analytical grade reagents and deionized water were employed to prepare all standards and sample solutions. Formic acid (CH_2O_2) at 88% (v/v) (JT Baker Chemical Company, Phillipsburg, New Jersey, USA), 65% (v/v) nitric acid (HNO_3) (Synth, Diadema, SP, Brazil) and 30% (m/m) hydrogen peroxide (H_2O_2) (Synth, Diadema, SP, Brazil) were used for sample preparation. The analytical calibration curves were prepared daily from 1000 mg/L stock solutions and ranged from 0.1 to 50 mg/L for both sample preparation methods. Liquid argon was used as purge and plasma gas (99.999% purity, White Martins, Sertãozinho, SP, Brazil). Three different certified reference materials (CRMs) were chosen to evaluate the trueness of the acid extraction procedure: bovine liver (NIST 1577b, Gaithersburg, MD, USA), apple leaves (NIST 1515, Gaithersburg, MD, USA) and whole milk powder (NIST 8435, Gaithersburg, MD, USA). All CRMs were kept in a desiccator with temperature and humidity controlled as recommended by the manufacturer.

2.3. Sample preparation for ICP OES determination

2.3.1. Formic acid extraction

The elements Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn were determined using ICP OES with dual view configuration. The formic acid extraction procedure consisted of the addition of 10 mL of 50% (v/v) formic acid to 150 mg of each sample. The flasks were placed on a heating block at 90 °C for 1 h and after the solution had cooled to room temperature, 2 mL of 30% (m/m) H_2O_2 was added and the flasks were heated again (1 h at 90 °C). After cooling to room temperature, the solution was transferred to volumetric vials and the volume was completed to 14 mL with deionized water. The samples were centrifuged for 5 min at 3500 rpm. Subsequently, an aliquot of each solution was appropriately diluted ($\sim 10 \times$ or $\sim 100 \times$) with deionized water, followed by quantification using ICP OES. All experiments were carried out in triplicate (n = 3).

2.3.2. Microwave-assisted digestion

A volume of 6 mL of HNO_3 (7 mol/L) and 2 mL of 30% (m/m) H_2O_2 were added to 150 mg of each sample in the microwave vessels. The microwave program used was: ramp of 1000 W for 5 min; 1000 W platform for 10 min; and 0 W for 20 min (Bizzi et al., 2014). After the vessels were cooled, the digests were transferred to a volumetric bottle and the volume was set to 14 mL with deionized water. An aliquot of each solution was appropriately diluted ($\sim 10 \times$ or $\sim 100 \times$) with deionized water, followed by quantification using ICP OES. All experiments were carried out in triplicate (n = 3).

3. Results and discussion

3.1. Method validation

The validation of the method was performed by calculating the accuracy of each element determined based on the certified reference values of the three CRMs used for the proposed method employing diluted formic acid sample preparation and a comparative method using microwave-assisted digestion with nitric acid. A paired t-test showed that the results for the determined elements concentrations, using formic acid for sample preparation was in most cases in agreement with the certified reference values, with a confidence interval of 95% according to the t-test (4.303). In some cases, the results were