



Evaluation of oxygen pressurized microwave-assisted digestion of botanical materials using diluted nitric acid

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ABSTRACT

The feasibility of diluted nitric acid solutions for microwave-assisted decomposition of botanical samples in closed vessels was evaluated. Oxygen pressurized atmosphere was used to improve the digestion efficiency and Al, Ca, K, Fe, Mg and Na were determined in digests by inductively coupled plasma optical emission spectrometry (ICP OES). Efficiency of digestion was evaluated taking into account the residual carbon content (RCC) and residual acidity in digests. Samples were digested using nitric acid solutions (2, 3, 7, and 14 mol L⁻¹ HNO₃) and the effect of gas phase composition inside the reaction vessels by purging the vessel with Ar (inert atmosphere, 1 bar), air (20% of oxygen, 1 bar) and pure O₂ (100% of oxygen, 1 bar) was evaluated. The influence of oxygen pressure was studied using pressures of 5, 10, 15 and 20 bar. It was demonstrated that a diluted nitric acid solution as low as 3 mol L⁻¹ was suitable for an efficient digestion of sample masses up to 500 mg of botanical samples using 5 bar of oxygen pressure. The residual acidities in final digests were lower than 45% in relation to the initial amount of acid used for digestion (equivalent to 1.3 mol L⁻¹ HNO₃). The accuracy of the proposed procedure was evaluated using certified reference materials of olive leaves, apple leaves, peach leaves and pine needles. Using the optimized conditions for sample digestion, the results obtained were in agreement with certified values. The limit of quantification was improved up to a factor of 14.5 times for the analytes evaluated. In addition, the proposed procedure was in agreement with the recommendations of the green chemistry once it was possible to obtain relatively high digestion efficiency (RCC < 5%) using only diluted HNO₃, which is important to minimize the generation of laboratory residues.

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1. Introduction

The determination of metals in botanical samples often requires a previous digestion step before analyte determination [1,2]. Closed vessels have been currently used in order to improve the oxidation efficiency and also to reduce the time of digestion. Although digestion using closed vessels may also employ conventional heating, most of the recent applications have been performed using microwave radiation in view of the relatively shorter time involved [3–5]. The possibility of working at high pressures in closed vessels causes an increase of the oxidant properties of nitric acid and for this condition the digestion of samples containing high content of organics can be carried out without addition of auxiliary reagents

[6–8]. However, for samples that present high content of silica and organic compounds (e.g., botanical samples) problems related to poor recoveries have been observed, mainly for elements associated with silicon present in plants such as Al and Fe [9]. Therefore, the additions of auxiliary reagents, such as H₂SO₄, H₂O₂, H₃BO₃, HF and HBF₄, are frequently necessary for a complete release of analyte to solution [9–11].

Nevertheless, the addition of auxiliary reagents for digestion increases the risk of contamination and may result in digests with high salinity and acidity that could not be suitable for conventional sample introduction devices used in some atomic spectrometry techniques [9]. In addition, the use of concentrated reagents is always hazardous, it requires dilution of the digests before the determination step and can generate high volumes of concentrated acids as effluents. In this way, the use of diluted acid solutions have been mainly reported for procedures employing microwave [12,13] and ultrasound energy [14,15] in order to obtain an improvement during extraction. This possibility of using diluted acid was observed during the use of microwave-assisted extraction for metal

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determination by ICP OES in raft mussels samples (up to 500 mg). Recoveries higher than 95% were obtained using 15 mL of a mixture of diluted HNO₃, HCl and H₂O₂ (2.5 and 3.0 mol L⁻¹ and 0.5%, respectively) for Ba, Cd, Cr, Cu, Fe, Mn, Pb, Sn, V and Zn determination. Quantitative recovery was obtained for Al only using a mixture of diluted HNO₃, HF and H₂O₂ (2.5 and 3.0 mol L⁻¹ and 0.5%, respectively) [16]. Microwave-assisted extraction using diluted solutions (10 mL of HNO₃ and HCl, 5–20%) was also used for Se determination by electrothermal atomic absorption spectrometry in medicinal plants (up to 200 mg). It was observed that under optimized conditions the results obtained for CRM samples showed agreement higher than 95% [17]. In the same way, procedures using ultrasound energy can be also employed to assist metal leaching using diluted solutions. It was observed during determination of As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, V and Zn in seaweed sample (up to 200 mg) using 7 mL of diluted solution of HNO₃, HCl and H₂O₂ (3.7, 3.0 and 3.0 mol L⁻¹, respectively) [18]. Determination of Cd, Cu and Zn in fish and mussel samples (up to 500 mg) by flame and graphite furnace atomic absorption spectrometry has been performed after ultrasound-assisted extraction procedure. Diluted solutions (6 mL) of HNO₃, HCl and H₂O₂ (4.0, 4.0 and 0.5 mol L⁻¹, respectively) were used and recoveries from 92 to 114% and from 88 to 103% were obtained for metal determination in fish and mussel samples, respectively [19].

In the same way, digestion procedure can be also performed using diluted acid solutions. Digestion procedures can minimize some drawbacks related to extraction procedure such as influence of particle size, the lack of accuracy for some elements and the complete dissolution of the analytes that must be ensured [12,14,15,18]. Performing reactions at high pressure and temperature may allow a reduction of the acid concentration without decreasing the efficiency of digestion. The feasibility of using diluted solutions containing lower concentrations of nitric acid has been experimentally demonstrated [20–22]. The efficiency of using diluted acids is a result of the temperature gradient inside the reaction vessel during the initial steps of sample digestion and due to the presence of a rich oxygen atmosphere inside the closed-vessel [22,23]. An important aspect is related to the poor absorption of microwave radiation by the gas phase that, despite this aspect, it can improve the oxidation processes. The combination of both effects results that reaction products can be oxidized also at the upper atmosphere of the reaction vessel and further reabsorbed in the liquid phase. Therefore, the use of oxygen atmosphere together with diluted nitric acid leads to a regeneration of nitric acid and to an improvement on digestion efficiency of samples [23].

Considering that sample matrix has a great influence on digestion efficiency and analyte recoveries the microwave-assisted digestion in closed vessels using diluted nitric acid within oxygen pressurized atmosphere was evaluated in the present work for botanical materials. The determination of Ca, K, Mg, Na, Al and Fe, elements that must be currently determined in plants, was performed by inductively coupled optical emission spectrometry (ICP OES) in oregano leaves and in botanical certified reference materials (CRM). In addition, it was tried to reduce as much as possible the amount of nitric acid needed for the digestion process in order to minimize the blank values and also decrease the consumption of reagents and the generation of laboratory residues.

2. Experimental

2.1. Instrumentation

A microwave oven (Multiwave 3000 microwave sample preparation system, Anton Paar, Graz, Austria) equipped with eight high-pressure quartz vessels was used in the experiments. The

Table 1

ICP OES operational parameters for determination of C, Al, Ca, Fe, K, Mg and Na.

Parameter	ICP OES
Radio-frequency power (W)	1600
Plasma gas flow rate (L min ⁻¹)	14.0
Auxiliary gas flow rate (L min ⁻¹)	1.0
Nebulizer gas flow rate (L min ⁻¹)	0.85
Spray chamber	Double pass, Scott type
Nebulizer	Cross-flow
Observation view	Axial
Emission line (nm)	
C (I)	193.091
Al (I)	167.078
Ca (II)	317.933
Fe (I)	238.204
K (I)	766.491
Mg (I)	285.213
Na (I)	589.592

internal volume of vessels was 80 mL and the maximum operational temperature and pressure was set at 280 °C and 80 bar, respectively. Pressure and temperature were monitored in each vessel for all the runs.

Analytes were determined by ICP OES using an axial view configuration spectrometer (Spectro Ciros CCD, Spectro Analytical Instruments, Kleve, Germany). Nebulization was performed through a cross-flow nebulizer coupled to a Scott double pass type nebulization chamber. Plasma operating conditions and selected wavelengths used for analytes determination are listed in Table 1, and they were used as recommended by the instrument manufacturer [24]. For the determination of residual carbon content (RCC, mg C/100 mg of sample) [25] digested solutions were determined by ICP OES [26]. In order to remove the volatile carbon compounds before RCC determination, samples were previously sonicated with a ultrasonic probe [27] (VCX 130 PB, 130 W, 20 kHz, Sonics and Materials Inc., Newton, CT, USA). Argon (99.996%, White Martins-Praxair, São Paulo, SP, Brazil) was used in ICP OES determinations for plasma generation, nebulization, auxiliary gas and also for digestion performed under inert atmosphere. Oxygen (99.9991%, White Martins-Praxair) was used as reagent in digestions performed under oxygen pressure.

Results for residual acidity were obtained using a titration system (Titrand 836, Metrohm, Herisau, Switzerland) equipped with a magnetic stirrer (module 803 Ti Stand), 20 mL burette (Dosino 800) and pH electrode (LL Electrode plus, model 6.0262.100).

2.2. Samples, reagents and standards

Preliminary experiments were carried out using the leaves of *Origanum majorana* (oregano) as sample, which was purchased in a local market. This sample was dried using an oven (model 400/2ND, Nova Ética, Vargem Grande Paulista, SP, Brazil) and ground using a cryogenic mill (Spex Certi Prep, model 6750, Metuchen, NJ, USA). The final particle diameter was below 102 µm. Accuracy was evaluated using a CRM of trace elements in olive leaves (BCR 62) produced by Community Bureau of Reference (BCR, Brussels, Belgium) and by using standard reference materials (SRM) of apple leaves (SRM NIST 1515), peach leaves (SRM NIST 1547) and trace elements in pine needles (SRM NIST 1575a), produced by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Samples were accurately weighed using an analytical balance (model AY 220, max. 220 g, 0.1 mg of resolution, Shimadzu, Kyoto, Japan).

Distilled-deionized water (Milli-Q, 18.2 MΩ cm, Millipore, Billerica, MA, USA) and analytical-grade nitric acid (Merck, Darmstadt, Germany) were used to prepare samples and standards. Carbon reference solutions used to external calibration for RCC deter-

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