Understanding the process of microwave-assisted digestion combining diluted nitric acid and oxygen as auxiliary reagent

Cezar A. Bizzi [a], Erico M.M. Flores [a], Juliano S. Barin [b], Edivaldo E. Garcia [c], Joaquim A. Nóbrega [d],*

[a] *Departamento de Química, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil and Instituto Nacional de Ciência e Tecnologia de Bioanalítica, Campinas, SP, Brazil*
[b] *Departamento de Tecnologia e Ciência dos Alimentos, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil*
[c] *Departamento de Química, Universidade Estadual de Maringá, 87100-900, Maringá, PR, Brazil*
[d] *Departamento de Química, Universidade Federal de São Carlos, 13565-905, São Carlos, SP, Brazil*

ARTICLE INFO

ABSTRACT

Sample preparation has a long history when thinking about the conversion of solid samples to representative solutions using concentrated acid solutions and high temperature. However, chemical sciences are evolving to cleaner procedures and surely, sample preparation must follow these steps. The advent of microwave-assisted digestion led to new devices that have allowed the development of new procedures based on diluted solutions of nitric acid and more recently the use of oxygen as a reagent. No doubts oxygen has played a major role in most dry and wet digestion procedures for digestion of organic samples, but its role was improved by using it to regenerate nitric acid and consequently decreasing the volumes of acids needed to promote efficient digestions. These aspects were clearly demonstrated by comparing the efficiency of whole milk powder digestions under different pressures of oxygen, atmospheric air or inert argon atmosphere. The pressure profiles in these conditions were also evaluated and indicate the regeneration process. The efficiency of the digestion process using oxygen was demonstrated by measuring residual carbon contents and residual acidity in digests and it was shown that both parameters were fully compatible with requirements of modern instrumental analysis without any further extensive dilution of the digestates.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Frequently the conversion of solid samples to representative solutions is one of the first steps in an analytical procedure and, even inside the chemistry community, it is considered as an art deeply rooted in alchemical knowledge. Maybe this notion comes from the advent of concentrated acids, which is one of the contributions of the alchemists to modern chemists. Therefore, it is still usual to think that sample digestion is just a question of adding huge volumes of concentrated acids to sample aliquots, followed by an increase of temperature to speed up oxidation of organic compounds and promote the rupture of chemical bonds. However, this paradigm is changing parallel to the advent of modern instrumentation that cannot cope with too concentrated acid solutions and because of the new technology for sample preparation based on microwave-assisted heating. Other force to push forward the knowledge about sample preparation and the development of softer procedure comes from the needs presented by green chemistry and speciation analysis.

Consequently, new devices and challenging demands must be followed by a new understanding of the sample digestion process.

Additionally, demands for green and safe methods must also be reached.

These forces have led to the development of sample digestion procedures using diluted solutions of nitric acid [1–3]. These studies proved the efficiency of diluted nitric acid solutions mainly when employing modern microwave reaction vessels [4] and it became clear that the temperature gradient inside these vessels plays a role in the process of regeneration of nitric acid. This is a critical aspect for the efficacy of the process and may help to understand why this was not made before. In other words, as recently demonstrated, the use of a vessel conductively heated and without temperature gradients, such as the high-pressure asher system, was not effective for promoting digestions when associated with diluted solutions of nitric acid [5]. Similar behavior was shown before by Korn et al. when comparing the efficiency of digestion with diluted nitric acid solutions in Parr bombs and in microwave vessels [4].

It was proposed that the regeneration of nitric acid is promoted by the oxidation of NO to NO_2 and the absorption of this later oxide in the solution followed by its disproportioning reaction [6]. If this is correct, the pressurization of the vessels with oxygen would improve further the digestion process. This aspect was recently proved by Bizzi et al. [7,8] and it was shown that the combination of diluted nitric acid solution plus oxygen pressurization allows to perform efficient digestions with solutions as diluted as 0.5 mol L^{-1} nitric acid. Of

course, this strategy is attractive to improve the power of detection and to decrease both the use of concentrated reagents and the generation of chemical residues.

These developments have at least two implications. One is the possibility of developing clean analytical procedures compatible with green chemistry and with modern instrumentation analysis. The other is the possibility of deepen the understanding of the chemical processes involved with the digestion, particularly for samples containing high contents of organic compounds.

This later aspect was here studied and it was systematically evaluated the influence of gas phase inside the reaction vessel by performing digestions under argon pressure and comparing it to digestions carried out under atmospheric air or oxygen pressure. Whole milk powder was chosen as a model sample for rich organic matrixes.

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

Residual carbon content (RCC) was determined by ICP OES [9,10] using an axial view configuration spectrometer with a cross-flow nebulizer coupled to a Scott double pass type nebulization chamber (Spectro Ciros CCD, Spectro Analytical Instruments, Kleve, Germany). Plasma operating conditions are shown in Table 1, and they were used as recommended by the instrument manufacturer [11]. In order to remove the volatile carbon compounds before RCC determination, sample aliquots were previously sonicated with a ultrasonic probe [12] (VCX 130 PB, 130 W, 20 kHz, Sonics and Materials Inc., Newtown, CT, USA).

Argon (99.996%, White Martins-Praxair, São Paulo, SP, Brazil) was used for ICP OES measurements and also for digestion performed under inert atmosphere. Oxygen (99.9991%, White Martins-Praxair) was used as reagent in digestions performed under oxygen pressure.

It is important to mention that all procedures under oxygen pressure were performed employing safety conditions, as recommended by the microwave oven manufacturer [13]. In addition, a procedure that uses an equivalent oxygen pressure is commercially available [14], which means that there is no risks in working under oxygen pressure up to 20 bar inside digestion vessel.

Results for residual acidity were obtained using a titration system (Titrando 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

Experiments were carried out using whole milk powder. Samples were 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 determination were prepared by dissolution of citric acid (Merck) in water (25 to 500 mg L^{-1} of C). Yttrium (1.0 mg L^{-1}, Spex CertPrep, Metuchen, NJ, USA) was used as internal standard in all samples, blanks and reference solutions for RCC determination. A 0.1 mol L^{-1} KOH (Merck) solution was used for residual acidity determination. Glass and quartz material were soaked in 1.4 mol L^{-1} HNO$_3$ for 24 h and further washed with water before use.

2.3. Microwave-assisted acid digestion

Masses of 500 mg of whole milk powder samples were transferred to the quartz vessels. Digestion efficiency using nitric acid solutions (6 mL) was evaluated in the following concentrations: 1, 2, 3, 7, and 14 mol L^{-1}. After closing and capping the rotor, vessels were pressurized with 2.5, 5, 7.5 and 20 bar of oxygen, which was introduced into the vessels using the valve originally designed for pressure release after conventional acid sample digestion. The same procedure was carried out with atmospheric air without pressure and, additionally, with Ar under pressure (20 bar). Then, the rotor was placed inside the oven, and microwave-heating program was started by applying (i) 1000 W with a ramp of 5 min, (ii) 1000 W for 10 min, and (iii) 0 W for 20 min (cooling step) [13]. After digestion, the pressure of each vessel was carefully released. In this work, each run was performed using a minimum of four vessels. The resulting solutions were transferred to 30 mL polypropylene vials and diluted to the mark with water. Cleaning of digestion vessels was carried out with 6 mL of concentrated HNO$_3$ in the microwave oven at 1000 W for 10 min and 0 W for 20 min for cooling.

3. Results and discussion

Preliminary experiments were performed using 500 mg of whole milk powder to evaluate the minimum nitric acid concentration that was sufficient to obtain suitable RCC values. According to the results obtained for RCC and residual acidity (Fig. 1) when digestions were performed under atmospheric air pressure, it was possible to achieve a minimum nitric acid concentration that led to proper organic matter digestion efficiency (7 mol L^{-1}, RCC lower than 12% m/m). Using 3 mol L^{-1} nitric acid solution, the digestion was not efficient (RCC>48% m/m) and final solutions were considered unsuitable to a

Table 1
Operational parameters for ICP OES.

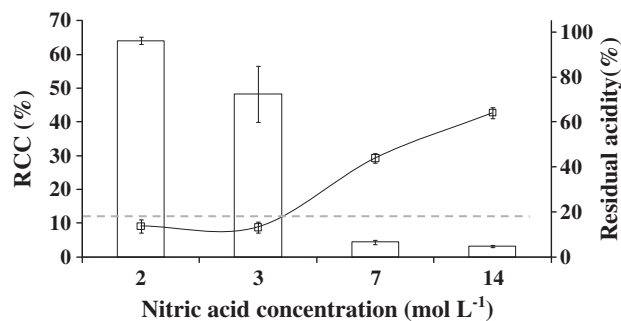| Parameter	ICP OES
Radio-frequency power (kW)	1.6
Plasma gas flow rate (L min^{-1})	14.0
Auxiliary gas flow rate (L min^{-1})	1.0
Nebulizer gas flow rate (L min^{-1})	0.85
Spray chamber	Double pass, Scott type
Nebulizer	Crossflow
Observation view	Axial
C (I) emission line (nm)	193.091

Fig. 1. Effect of nitric acid concentration on digestion of 500 mg of whole milk powder; effectiveness of organic matter digestion (white bars) and residual acidity (-□-) performed at atmospheric air (1 bar). Horizontal gray line represents the selected tolerance level of RCC (12%). Error bars represent the standard deviation (n = 3).