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Experimental design in the optimization of a microwave acid digestion procedure for the determination of metals in biomorphic ceramic samples by inductively coupled plasma mass spectrometry and atomic absorption spectrometry

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ABSTRACT

In the present paper, we have synthesized a biomorphic ceramic material from oak wood as biological template structure and infiltration with zirconia-sol. After the material characterization, we have optimized the sample dissolution by acid attack in an oven under microwave irradiation. Experimental designs were used as a multivariate strategy for the effect's evaluation of varying several variables. This article describes the development by response surface methodology (RSM) of a procedure for zirconium determination, and other ions, such as copper and nickel by inductively coupled plasma mass spectrometry (ICP-MS) and others, such as iron, calcium and magnesium determination by flame atomic absorption spectrometry (FAAS) in the synthesized sample after digestion. A full factorial design (3^3) was used to find optimal conditions for the procedure through response surface study. Three variables (time, HNO_3 volume and HF volume) were regarded as factors and as response to the concentration of different metal ions in the optimization study.

1. Introduction

Sample preparation is the critical step of any analytical protocol, and involves steps from simple dilution to partial or total dissolution. The methods include dry or wet decomposition of the samples in open or closed systems, using thermal, ultrasonic or radiant (infrared, ultraviolet and microwaves) energy. Microwave-assisted sample preparation is now used for a wide range of applications, including decomposition of inorganic and organic materials [1–3].

Microwave digestion involves the use of 2450 MHz electromagnetic radiation to dissolve samples. The rate of microwave digestion is dependent on the coupling efficiency of microwaves with digestion acids. Microwave technology is often recommended for safety considerations. They are also programmable and can accommodate large numbers of samples [4,5].

Microwave-assisted digestion has clear advantages over the traditional acid digestion using convective heating systems in terms of recovery, precision, short time needed (minutes) to perform decomposition of the sample, direct heating of samples and reagents (the vessels are only indirectly heated by the hot solution), minimal contamination and losses of volatile elements. It reduces the possibility of cross contamination and the consumption of reagents. The use of small amounts of reagents decreases the blank signal. The combination of different acids, such as H_2SO_4, HNO_3, HCl and HF is a very frequent method for preparing samples before their quantitative elemental analysis.

The proposal of a new analytical method requires the optimization of the experimental variables that involves the selection of the values of the factors that have an influence on the analytical signal and lead to the best results for the analytical process. The optimization of the proposed method allows us to understand the effects that are not explained in a traditional way, such as those in which the analytical response is a multimodal function of the independent variables or when the effects of the variables are not additives and there is interaction among them. The association of factorial design and microwave-assisted digestion can contribute to accelerate the sample pre-treatment step, improving the accuracy of the results. On the other hand, ICP-MS is an ideal technique for determining elements, with rapid data acquisition and low detection limits. In this context, two methods were reported for the preparation of geological samples using microwave digestion prior to determination of the platinum-group elements and Au by ICP-MS [6,7]. Uchida et al. [8] carried out a comparison of alkaline fusion and acid digestion methods for the determination of rhenium in rock and soil samples by ICP-MS. Hassan et al. [9] developed an analysis of environmental samples using microwave-assisted acid digestion and ICP-MS. Recently, a method using microwave digestion combined with ICP-MS was described to analyze the elemental composition of a variety of komatiites samples [10] (an important rocky component of the primitive environment in the early Earth and, as well a possible extraterrestrial planetary volcanic

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material [11]) and a microwave-assisted digestion method amenable to analysis of small size biological samples has been optimized for determining twelve elements by ICP-MS [12].

With respect to zirconium determination by ICP-MS in different samples, for example, a technique for the determination of titanium and zirconium in human blood serum, after pressurized digestion utilizing ICP-MS coupled to an ultrasonic nebulizer and desolvating membrane is described by Kunze et al. [13], a method is described for the determination of Nb, Ta, Zr and Hf at low levels in geological materials [14] and a simultaneous preconcentration and determination of ultratrace Zr, Hf, Nb, Ta and W in seawater is presented by Firdaus [15].

On the other hand, biomorphic ceramics are a class of materials produced with natural, renewable resources (wood or wood-based products). These materials can be used for a variety of applications including filters and catalyst support, automotive components, tooling and wear components, armor and lightweight, porous ceramics for aerospace systems. Wood is an excellent example of naturally optimized structural material which combines light weight, highly directed porosity and a large surface area with a high specific strength. The approaches to convert the native wood into ceramic products include: (i) pyrolytic decomposition resulting in a porous carbon replica; (ii) infiltration of biocarbon template with gaseous or liquid precursors and subsequent to form non-oxide as well as oxide ceramic via reactive or molding techniques. The recent progress in the synthesis of wood-derived ceramics from natural templates is summarized by Luo et al. [16]. During the last decade several investigations were focused on the synthesis of biomorphic non-carbide materials. Vacuum infiltration with different sols, pyrolysis in inert atmosphere and subsequent annealing in air resulted in the formation of porous Al_2O_3, TiO_2, $Al_6Si_2O_{13}$ and ZrO_2 ceramics [17]. Singh and Yee [18] infiltrated jelutong wood with ZrO_2 sol for manufacturing of monoclinic ZrO_2 ceramics with biomorphous structure. Cao et al. [19–22] prepared biomorphic Al_2O_3, TiO_2 and ZrO_2 ceramics from pine wood as well as TiO_2 ceramics from cellulose fibber pre-forms via a sol–gel process with metal alkoxides.

This work proposes the use of factorial design for optimization of microwave-assisted digestion of biomorphous ZrO_2-ceramic synthesized by us previously. The accuracy of digestion procedures is affected by critical experimental parameters, such as concentrated acid volumes and digestion time. The effects of these key variables on the microwave-assisted digestion efficiency were investigated. The determinations of elements in the digests were performed using ICP-MS and FAAS.

2. Experimental

2.1. Instrumentation

A Lenton Tube furnace, model LTF 16/180, was employed for the synthesis of biomorphic ceramics.

Table 1
ICP-MS operating parameters used for element determination.

RF power	1100 W
Nebulizer gas flow	0.92 L min^{-1}
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1.2 L min^{-1}
Nebulizer	Cross-flow
Spray chamber	Scott type
Cones	Nickel
Lens voltage	6.5 V
Analog stage voltage	−1800 V
Pulse stage voltage	850 V
Sweep/reading	20
Reading/replicate	1
Replicate	3
Scan mode	Peak hopping

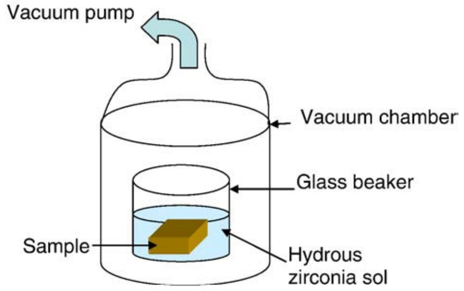

Fig. 1. Schematic drawing of the experimental set-up for the vacuum infiltration process.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Physical Electronics 5700 instrument with a Mg $K\alpha$ X-ray excitation source ($h\nu = 1253.6$ eV); binding energies (BE) were determined with respect to the position of the C1s peak at 284.5 eV. The residual pressure in the analysis chamber was maintained below 133×10^{-9} Pa during data acquisition.

A Panasonic (National) microwave oven, model NN-8507, and a Parr Microwave Acid Digestion Bomb, model 4782, were used for sample digestion. The bombs were cleaned before use with 10% (v/v) HNO_3 for 1 day followed by repeated rinsing with water.

A Varian Model SpectrAA 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer (FAAS) was used for the Ca, Fe and Mg analysis with the appropriate hollow cathode lamp.

The measurements of Cu, Ni, and Zr elements were performed on a PerkinElmer ELAN DRCe ICP-MS quadrupole spectrometer. The samples were introduced into the ICP-MS via a RytonTM cross-flow nebulizer (PerkinElmer), Scott spray chamber (PerkinElmer) and Cetac ASX-510 autosampler. The sample transport from the autosampler to the nebulizer was established by a peristaltic pump. The operating parameters of the spectrometer are summarized in Table 1.

2.2. Reagents

Analytical reagent grade chemicals were used throughout. $ZrOCl_2.8H_2O$ (Merck). Standard 1000 µg mL^{-1} Zr(IV), Cu(II), Ni(II), Fe(III), Ca(II) and Mg(II) solutions (Fluka) were used. Standards of

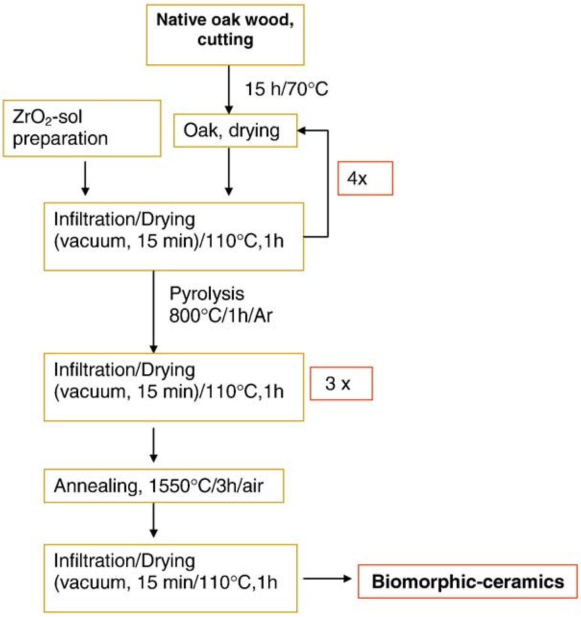

Fig. 2. Flow chart for the manufacturing of biomorphic ZrO_2 ceramics.