Multivariate optimization of the synthesis and of the microwave dissolution of biomorphic silicon carbide ceramics

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ABSTRACT

Biomorphic silicon carbide ceramics are a new class of materials that are used for various industrial applications owing to its attractive properties. The efficiency of the synthesis and the partly extreme properties of the biomorphic ceramic depend decisively on the synthesis parameters and on the impurities of the final ceramic. In the present article the synthesis as well as the decomposition of these materials is optimized using a multivariate methodology for the design of experiments. Three variables (initial amount of Si, infiltration temperature and reaction time) were considered as factors in the synthesis optimization and six variables (digestion time, ramp time, microwave power, volumes of concentrated HF, HNO_3 and H_2SO_4) in the microwave dissolution optimization. Interactions, between analytical factors and their optimised levels were investigated using full factorial, Plackett–Burman and central composite designs. The synthesis parameters that found higher percentage of SiC (quantified by FTIR) and the digestion procedure that found higher concentrations of metals (Co, Cr and Ni, determined by FI-ETAAS) were considered the optimum.

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1. Introduction

Biomorphic ceramics are materials made by a transformation of biological preforms into a ceramic material. Different applications are promising for such materials, especially for SiC ceramics, because of their good performance, including high-temperature stability, high mechanical strength, high thermal conductivity and chemical inertness towards acids and bases [1–3]. These materials are used in structural applications (machine and cutting tools, wear components, aerospace components, and biomedical implants) and in electronic applications (insulators, capacitors, transducers, electronic sensors, and electrooptical elements).

The synthesis of these new materials is based on the infiltration of the pyrolyzed wood templates with silicon; there are several ways of synthesis: infiltration with molten silicon [4–7], chemical Si contained vapor infiltration (CVI) [8,9], infiltration–pyrolysis of metallic-alkoxide [10], polymeric precursors [11], sol–gel infiltration/carbothermal reduction [12–14], etc. Between them, the chemical vapour infiltration produces SiC ceramics with very good properties; however, the cost is high compared with the infiltration with molten silicon. In this last technique, biomorphic SiC ceramics are made by a two step process: a controlled pyrolyzation of the wood followed by a rapid controlled reactive infiltration of the wood preform with molten silicon. The diversity of wood species provides a wide choice of

materials, in which the density and the anisotropy are the critical factors of the final microstructure and hence of the mechanical properties of the material. This manufacturing process presents several advantages over others: lower cost reduces the temperatures of process and the use of additives or high purity powders and faster, because the time and the synthesis rates are reduced.

The properties of these materials are greatly influenced by the stoichiometric molar ratio of the macroconstituents, and also by the presence of impurities [15], even at very low concentrations. Furthermore, small amounts of dopants [16], sintering aids [17] and other additives are added to these ceramics in order to improve their processing and ultimate properties. Because of this, the determination of elements in advance ceramics is crucial to manufacturing control, property improvement, failure prevention and quality assurance. However, the chemical composition of the biomorphic materials has been scarcely investigated. For the chemical analysis of these refractory and chemically resistant materials by atomic spectrometry, complete dissolution of the samples with extreme chemical treatments must be performed. The microwave-assisted pressure digestion is a promising alternative for sample preparation owing to the advantages over acid decomposition and alkaline fusion procedures: strict control of the heating power, ability to use small volumes of reagents, lower reagent blank, etc. Matusiewicz [18] evaluated a commercial laboratory microwave acid digestion system for the acid dissolution of ceramic powders (Al_2O_3, AlN, BN and Si_3N_4) prior to the determination of their trace element content by microwave induced plasma atomic emission spectrometry. Mann et al. [19] compared various wet chemical digestion procedures, such as pressure

digestion, microwave-assisted pressure digestion and decomposition via alkaline fusion for the dissolution of new advanced ceramic materials, with subsequent determination of the main components Si and B by sequential inductively coupled plasma atomic emission spectrometry (ICP-AES). Larrea et al. [20] compared the detection limits obtained for some elements by ICP-AES in the dissolution of electronic advanced ceramics by acid microwave-assisted heating and alkaline fusion. Also they compared the analytical results obtained in the determination of impurities by ICP-AES in a lead titanate-based ceramic. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most popular techniques for ultra-trace analysis owing to its high sensitivity and low detection limit. Applications of ETAAS are found in analyzing industrial materials such as silicon dioxide powder [21]. However, matrix interferences and/or a very low analyte concentration usually cause difficulties in the direct measurement of the analyte. The coupling of flow injection (FI) on-line column preconcentration/separation techniques to ETAAS has proved to be effective for this purpose [22]. Experience in our laboratory and the consulted bibliography [20,23] has shown that for the dissolution of materials with high levels of Si (SiC), the mixture of $HNO_3 + H_2SO_4 + HF$ under microwave-assisted pressure digestions can be used.

In the present work, we have optimized the experimental conditions for the synthesis and for the dissolution of this type of materials. The procedures were optimized by resorting a full factorial design for the synthesis [24]; and a Plackett–Burman screening design [25] and central composite design (CCD) [26,27] for the microwave dissolution. For the evaluation of the quality of the process of synthesis of these biomorphic ceramics, SiC was quantified in the synthesized ceramics by Fourier transform infrared spectroscopy (FTIR) [28]. For the optimization of the microwave-assisted pressure digestion, a FI on-line column preconcentration system coupled to ETAAS was developed in this work for the determination of the low concentrations of cobalt, nickel and chromium present in the biomorphic ceramics. Three variables (initial amount of Si, infiltration temperature and infiltration time) were considered as factors in the synthesis optimization and six variables (digestion time, ramp time, microwave power, volumes of HF, HNO_3 and H_2SO_4) in the microwave dissolution optimization. The variables that did not have a significance effect on the responses were screened out, and the remaining factors affecting the procedures were optimized using a CCD. This type of design allows the experimental domain to be mapped and optimal values for parameters to be deduced, while reducing the number of experiments compared to a sequential design. Understanding the main factors and their interactions permitted the development of a mathematical model to predict instrumental response.

2. Experimental

2.1. Reagents and samples

High-purity reagents were employed in all experiments. The KBr pellets were prepared with potassium bromide and barium acetate from Merck (Darmstadt, Germany). Pure silicon and silicon carbide (99.999%, w/w) were purchased from Aldrich Chemie (Steinheim, Germany). All these reagents were dried at 48 °C for 24 h and after conserved into a desiccator. Analytical reagent grade HNO_3 (65%), H_2SO_4 (97%), and HF (48%) (Merck, Darmstadt, Germany) were used as reagent for dissolution procedures. Doubly deionised water with a resistivity 18.2 MΩ cm^{-1}, produced by a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout. Standards solutions 1000 µg ml^{-1} Co, Ni and Cr (Fluka, Buchs, Switzerland) were used. Standards of working strength were made by appropriate dilution as required, immediately prior use. Ascorbic acid (Merck) 1000 µg ml^{-1} was used for cobalt determination. A pH 8.5 buffer was prepared by mixing boric acid (Merck) 0.2 M with NaOH (Merck) until pH 8.5 was reached.

Different kinds of biomorphic ceramics derived from natural woods (oak, beech, Swedish pine and eucalyptus) have been used. The synthesis and characterisation of 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide (DPTH-gel) chelating resin were described in a previous paper [22]. Argon with a purity of 99.99%, was used as the internal gas during analysis and synthesis of the biomorphic ceramics.

2.2. Instrumentation

The infrared spectroscopic measurements were carried out using a Shimadzu Model 8300 Fourier transform infrared spectrometer. The spectra were recorded in the range 2000–500 cm^{-1} with a resolution of 2 cm^{-1}. Potassium bromide pellets were used to obtain the IR spectra of the samples. The pellets with 13 mm diameter and 0.4 mm thickness were pressed at 8 tonnes for 10 min in an evacuated pellet die from 90.0 mg mixture sample, barium acetate and potassium bromide. For the mass measurements an AND GR-202 balance was used with a precision of ± 0.01 mg. Multivariate calibration data was carried out using Statgraphics Plus 6.0 professional software [29].

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

The ETAAS measurements were carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman/4100ZL, atomic absorption spectrometer with a longitudinal Zeeman effect background correction system, equipped with an AS-70 furnace autosampler. The standard transversely heated graphite atomizers (THGA) with integrated pyrolytic graphite platforms were used. Cobalt, nickel and chromium cathode lamps (Perkin-Elmer) were used at a wavelength of 240.7, 232.0 and 357.9 nm, respectively, with a spectral bandpass of 0.7 nm for Cr and 0.2 nm for Co and Ni.

The samples were digested using an Anton Paar (Graz, Austria) Multiwave 3000 microwave oven equipped with a XF-8 rotor and XF-100 digestion vessels. After digestion the solutions were evaporated into the EVAP rotor.

The microcolumn containing the DPTH-gel was a glass tube (3 cm × 3 mm i.d.) packed to a height of 0.5 cm; at both ends of the microcolumn, polyethylene frits (Omnifit, Cambridge, UK) were fixed to prevent material losses. On the end of this column was placed a piece of sample capillary of the sampler arm (in imitation of the sample tip of the sampler arm). Thus the sample tip of the sampler arm was replaced with this microcolumn. This connection is extremely simple, and permits full use of the original software. A peristaltic pump (Gilson Minipuls 3, Williers, France), fitted with a vinyl pump tube (1.65 mm i.d.) was used for loading of the sample. A Rheodyne (Cotati, CA, USA) Type 50 six-port rotary valve was used as a switching valve. Transport lines were made using 0.5 mm i.d. Teflon tubing. A schematic diagram of the circuit and peripherals was shown in a previous paper [30].

2.3. Synthesis of the biomorphic ceramics

Rectangular specimens of wood (beech) were cut with dimensions of (15 mm × 10 mm × 10 mm) in axial orientation. The carbon performs were prepared by pyrolyzing the dried (70 °C, 15 h) wood in argon-atmosphere. A slow heating rate of 1 °C/min was applied up to 500 °C where the organic biopolymers have been completely decomposed to carbon followed by an accelerated rate of 5 °C/min up to 1000 °C. This temperature was held for 4 h, resulting in a porous biocarbon template (charcoal). Each charcoal was placed in a boron nitride-coated alumina crucible with an appropriate amount of silicon powder. Compared to the carbon, the silicon was in molar excess up to a factor of 2.5 to aid in the conversion of the charcoal to SiC. Carbon and silicon were heated in vacuum to a temperature higher than 1410 °C at which point the silicon became molten and was wicked into the porous carbon template. The system was held at that temperature for different times to allow the reaction to progress. The

Table 1
Optimum operating conditions for the sequential determination of cobalt, nickel and chromium.

FI system	
pH of the sample	8.5
Sample loading time	30 s for Cr and Ni; 120 s for Co
Sample flow rate	2 ml min^{-1}
Eluent	HNO$_3$ 2 M, (20 µl for Co and Ni; 40 µl for Cr)

Graphite furnace temperature program				
Stage	Parameters			
	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow rate (ml min^{-1})
1	125	1	30	250
2	330	10	25	250
3	1050 (Ni) 1500 (Cr, Co)	10	25	250
4	2300 (Ni, Cr) 2500 (Co)	0	5	0 read (peak height)
5	2500	1	5	250

final optimum conditions for the synthesis were: amount of Si, molar excess of 2.5, infiltration temperature, 1600 °C and infiltration time, 300 min.

2.4. FTIR SiC determination

The yield of the synthesis was quantified by the determination of SiC in the synthesized ceramics through Fourier transform infrared spectroscopy. The procedure was based on the use of the ratio between the absorbance of the characteristic band of silicon carbide and those of acetate, used as internal standard. A multivariate calibration strategy based on inverse least squares and the standard addition approaches was employed. The method was described in a previous work [28].

2.5. Microwave dissolution process

The biomorphic materials were powdered and homogenized in an agate mortar, after which an accurately weighed amount of 10 mg was subjected to microwave digestion as follows: different volumes of concentrated HNO$_3$, H$_2$SO$_4$ and HF were added to the weighed amount of sample into a digest vessel, then this vessel was put into the microwave oven at different power, ramp and digestion times. At the end of the digestion program the vessels were allowed to cool before removing them from the microwave unit (25 min). After digestion, the solutions were evaporated to a small volume in order to eliminate the excess of acids, the pH of the solutions was adjusted to 8.5 with concentrated NaOH and buffer solutions, finally the samples were diluted to 100 ml with de-ionized water in a calibrated flask. Blanks were prepared in a similar manner. Samples were analyzed immediately after preparation, by introducing them into the FI manifold described previously [30]. The final optimum conditions adopted in the digestion procedure were: reagents, 6.6 ml concentrated HNO$_3$ + 7.8 ml concentrated HF + 4.0 ml concentrated H$_2$SO$_4$, microwave program, power 1400 W, hold time 60 min, ramp time 2 min.

2.6. On-line preconcentration/separation and determination procedure

The on-line FI system for ETAAS and experimental procedure described previously [30] was used in this work. The optimum working conditions optimised for the determination of nickel, cobalt and chromium in biomorphic ceramic materials are summarized in

Table 1. All the determinations were performed by using standard addition for calibration, in triplicate.

2.7. Experimental designs

For the experimental design modelling, programs from Statgraphics Plus Version 6.0 [29] were used.

2.7.1. Optimization strategy

Three variables (initial amount of Si, infiltration temperature and reaction time) were considered as factors in the synthesis optimization. These variables were optimized by a full factorial design with three center points [24]; which correspond to three factors at two levels ($2^3 = 8$ experiments + 3 center points = 11 experiments or runs). Such an experiment allows studying the effect of each factor on the response variable (%SiC in the synthesized ceramic, determined by FTIR as described in elsewhere [28]), as well as the effects of interactions between factors on the response variable. The selected factors and their corresponding levels appear in Table 2.

To find the main factors affecting the digestion procedure two level Plackett–Burman design [25] with 12 runs was used. All experiments were randomly performed without replication. The significance of the effects was made by Analysis of the Variance (ANOVA) and using p-value significant levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the p-value is less than 5%, the effect of corresponding factor is significant. The selected factors and their corresponding levels appear in Table 4.

The variables that did not have a significant effect on the responses (standard-to-blank ratio for Co, Cr and Ni) were screened out, the remaining factors affecting the digestion procedure for each analyte were simultaneously optimised by application of a central composite design plus face centred star (CCD) [26,27]. The three factors CCD used in this investigation included a total of $2^k + 2k + n$ runs (22 experiments), where k is the number of studied factors, 2^k are the points from the factorial experiments carried out at the corners of the cube (8 experiments) and 2k are the points carried out on the face centred star (six experiments); n, number of experiments carried out at the centre of the experimental domain was fixed at 8. The repetition of the centre points was used to estimate the experimental error.

2.7.2. Mathematical model

CCD provides sufficient data for linear polynomial models to be fitted to data sets for the three mentioned analytes. These models are

Table 2
Variables and their levels in the synthesis optimization.

Variable	Low (−)	High (+)
Si/C molar ratio	1.00	2.50
Infiltration temperature (°C)	1410	1600
Infiltration time (min)	30	240

Design matrix and response values obtained in the factorial design			
Experiment number	Si/C molar ratio	Infiltration temperature (°C)	Infiltration time (min)	SiC yield (%)
1	2.50	1410	30	3 ± 1
2	1.00	1410	240	18 ± 11
3	1.75	1500	135	33 ± 3
4	1.75	1500	135	33 ± 6
5	2.50	1600	240	80 ± 10
6	1.00	1410	30	9 ± 8
7	2.50	1410	240	60 ± 26
8	1.00	1500	30	7 ± 3
9	1.00	1600	240	49 ± 15
10	2.50	1600	30	39 ± 5
11	1.75	1500	135	34 ± 2

amenable to regression analysis. For three factors, the polynomial for given studied specie takes the form

$$y = \beta_0 + \sum \beta_j x_j + \sum \beta_{jj} x_j^2 + \sum \beta_{jk} x_j x_k$$

Where y is the response (peak area), x_{jk} are the variables of system and β_0, β_j, β_{jj} and β_{jk} are the regression coefficients for constant, linear square and interaction terms, respectively. The β coefficients represent the parameters of the model which are interactively optimised. These coefficients are calculated by fitting the value of experimental parameters to the least squares regression line. A quadratic equation or an equation containing only significant terms results is obtained. This can then be used to predict the response of the system at given levels of experimental factors.

3. Results and discussion

3.1. Optimization of the synthesis of the biomorphic SiC ceramics

3.1.1. Selection of the precursor materials

Given the myriad of wood in existence, there is a wide range of densities, cell sizes, and cell size distributions to choose from when selecting precursor. Wood can be classified as either softwood or hardwood. Softwoods (e.g. pine or eucalyptus) have one type of pore in the plane perpendicular to the growth direction (axial plane) while hardwoods tend to have two types of pores in this plane. In hardwoods, the smaller pores with thicker cell walls are referred to as fiber cells which provide strength to the tree. The larger pores with thinner cell walls are referred to as sap channels which allow the conduction of fluids throughout the tree. The hardwoods with uniformly distributed small sap channels can be referred to as uniformly distributed pore (UDP) hardwoods (e.g. beech) and the hardwoods with relatively large sap channels that are not uniformly distributed can be referred to as not uniformly distributed pore (NUDP) hardwoods (e.g. oak) [31]. It has been found that hardwoods UDP with smaller pores uniformly distributed show higher conversion to SiC. The only necessary condition is that the wood material presents a minimum porous size about 5 μm for efficient infiltration [32].

In this study beech wood was chosen as precursor. Beech wood is a UDP hardwood with relatively low density, 0.76 g cm⁻³ and has already been used in several studies [28,31,33–35]. The wood pieces were cut in axial orientation according to the direction of length perpendicular to the direction of wood growth. Infiltrations in axial direction show a higher SiC conversion due to easier transport of liquid silicon through the channels of the carbon perform [36].

3.1.2. Selection of the factors in the synthesis optimization

Three variables (initial amount of Si, infiltration temperature and time) were considered as factors in the synthesis optimization. The studies provided by Hou et al. [34] showed that the key factors affecting properties of the resulting biomorphic SiC ceramics were conversion degree and the amount of the residual silicon. According to the reaction equation of C and Si, pure SiC can be obtained when the weight ratio of starting silicon powder to biocarbon is about 2.34, that is, a molar ratio of 1. Hou et al., observed from the X-ray diffraction (XRD) pattern of the biomorphic SiC that the resulting product may consist of pure SiC phase when the weight ratio Si/C was in the range 3–4. With increasing starting Si contents, the porosity decreased and the bending strength and fracture toughness enhanced. In this work the initial amount of Si was varied between Si/C molar ratio 1 to 2.5 (weight ratio 2.34 to 5.83).

For a good and spontaneous infiltration process, Si must present an adequate viscosity and permeability. The Si melt point is 1410 °C, so this was the minimum temperature chosen, and the maximum was

1600 °C, imposed by the characteristics of the furnace employed for the synthesis.

Infiltration time is an important factor to fabricate biomorphic ceramics with various strengths and open porosity. With prolonging reaction time, the resulting products change from biocarbon to biomorphic C/SiC, and then to SiC/Si. The porosity decrease and the bending strength and fracture toughness enhanced as reaction time prolongs [33]. In the bibliography data are found since 30 min [6], 60 min [31,35], 90 min [34] to 180 min [36]. Due to the diversity of studies, this variable was varied between 30 to 240 min.

The selected factors and their levels are shown in Table 2.

3.1.3. Factorial design

Two level factorial designs have many advantages, for example they are more efficient than studying one factor at a time. A factorial design allows the effect of several factors and even interactions between them to be determined with the same number of trials as are necessary to determine any one of the effects by itself with the same degree of accuracy.

A two level full factorial design with three center points [24]; which correspond to three factors at two levels ($2^3 = 8$ experiments $+ 3$ center points $= 11$ experiments or runs) was used to optimize the synthesis of the biomorphic SiC ceramics. Such an experiment allows studying the effect of each factor on the response variable (%SiC in the synthesized ceramic), as well as the effects of interactions between factors on the response variable. The selected factors, their corresponding levels, the experimental design matrix developed and the results obtained as % SiC in the synthesized ceramic in each experiment are shown in Table 2.

The significance of the effects was checked by analysis of the variance (ANOVA) and using P-value significance levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the P-value is less than 5%, the effect of the corresponding factor is significant. According to ANOVA data, Pareto and main effects graphs (Fig. 1) all the factors studied were significant, with a positive effect on the SiC yield. The interaction between the initial amount of Si and the infiltration time was also significant. When the initial amount of Si is higher, the necessary time for the complete infiltration is higher too.

Thus, the optima conditions for the synthesis were the maxima values studied for the factors: initial amount of Si molar ratio Si/C = 2.5, infiltration temperature 1600 °C and infiltration time 240 min.

In order to verify the conclusions obtained from experimental design a new experiment was performed by increasing only one of three factors involved in the process that could be increased: infiltration time. As the temperature of 1600 °C is the maximum that the furnace can reach and if the initial amount of silicon increases, the infiltration time would be increased still further.

Then, for a Si/C molar ratio 2.5, infiltration temperature 1600 °C and infiltration time 300 min, a calibration line was prepared by addition of 0.00 to 2.50 mg SiC to the biomorphic ceramic synthesized. The peak area values of the interest bands were calculated using the baselines given in Table 3. The observed versus predicted graph and the equation of the fitted model for the biomorphic ceramic for SiC determination are given in Fig. 2. The SiC yield obtained for this experiment was $90 \pm 8\%$, very close to 100% of infiltration.

3.2. Optimization of the on-line preconcentration/separation and determination procedure

Since the solution pH affects the extent of complexation with DPTH-gel, which in turn determines the percentage of metal retained by the resin, the preconcentration of the metallic ions from solutions buffered at different pH was studied. The pH was adjusted from 2.0 to 5.0 using sodium acetate–acetic acid buffer and from pH 5.0–11.0
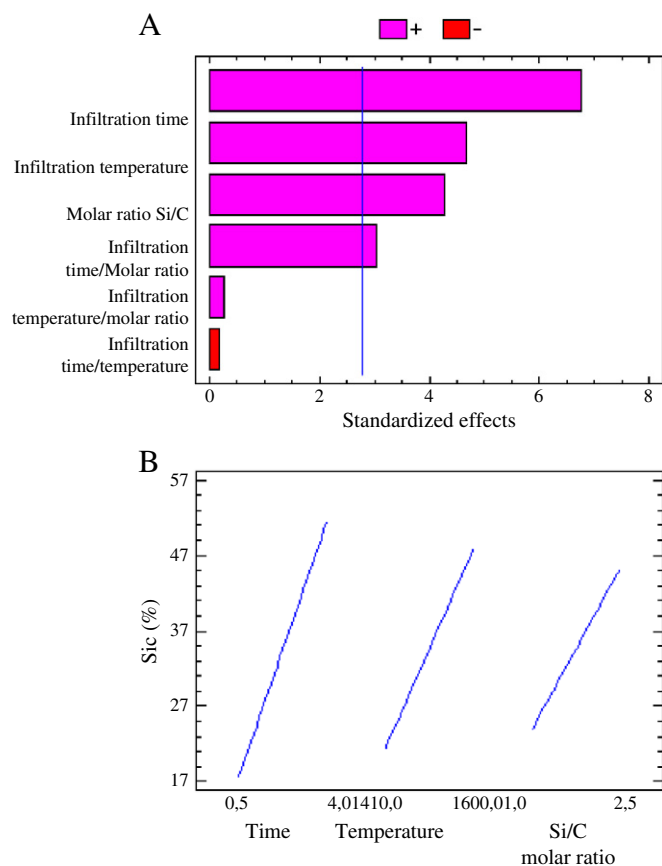
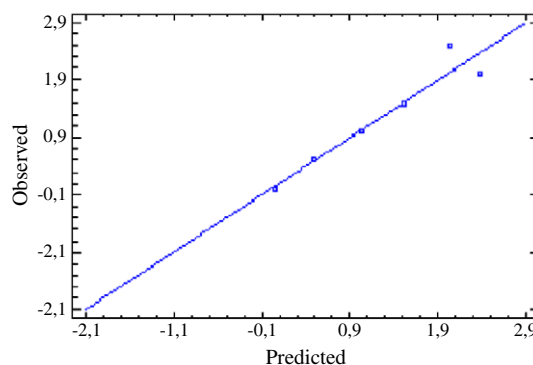**Fig. 1.** Standardized pareto chart (A) and main effects plot (B).

Fig. 2. The observed vs. predicted graph of the fitted model for the biomorphic ceramic for SiC determination.

of analyte giving signals equivalent to three times the standard addition of the blank plus the net blank intensity, were 0.20; 0.14 and 0.06 ng ml^{-1} for Co, Cr and Ni, respectively.

3.3. Optimization of the sample digestion procedure

Decomposition time depends on the acids used, the temperature, the pressure, the surface area of the sample material, its grain size and sometimes also on the purity of the powders [18]. Experience in our laboratory and the consulted bibliography [20,23] has shown that for the dissolution of materials with high levels of Si (SiC), the mixture of $HNO_3 + H_2SO_4 + HF$ under microwave-assisted pressure digestions can be used.

In developing the digestion procedure, one needs to adjust many variables: volumes of HF (factor A), HNO_3 (factor B) and H_2SO_4 (factor C), microwave power (factor D), digestion time (factor E) and ramp (factor F). This can be very time-consuming if a conventional univariate optimisation is undertaken manually and, where interactions exist between the variables, one is unlikely to find the true optimum. For these reasons, the optimization of the procedure was carried out by applying the experimental design methodology. This multivariate optimization implies two steps: (i) a preliminary evaluation, using screening factorial designs, in order to select the significant factors in the analytical procedure, and (ii) an appropriate estimation of the real functional relationship (response function) between the analytical response and the significant factors, obtaining from it the optimum values for these factors.

To find the main factors affecting the digestion procedure two level Plackett–Burman design [25], $2^6 \ast 3/16$ with 12 randomised runs and five degrees of freedom were carried out using Statgraphics. The significant of the effects was made by ANOVA and using p-value

using borax–boric acid buffer. As can be seen in Fig. 3 the optimum pH range for the quantitative retention of the three metals was around 7.5–8.5.

Chemical parameters, as well as the analytical flow system, which was coupled on-line to the preconcentration and separation unit, were optimized in order to obtain high sensitive, accurate and reproducible results for the three metal ions. The final conditions adopted in this study are given in Table 1. For cobalt determination 5 μl modifier solution (ascorbic acid) was added before injection of the sample into the graphite furnace.

As for graphite temperature program: complete dryness of aqueous standards and samples was ensured with two drying steps at 125 and 330 °C (slightly superior to the temperature of boiling of sulphuric acid); a ramp of 10 s for the second drying temperature at 330 °C avoided spattering of the liquids and resulted in a uniform solid deposit on the surface of the atomiser platform. The rest of the graphite operating conditions was optimized by a univariated form taking the sample-to-blank ratio as the election criteria. The optimized furnace temperature programs for Cr, Ni and Co determination in biomorphic ceramics are given in Table 1. Under the optimum conditions the detection limits, defined as the concentration

Table 3

Baseline established for integrating areas in FTIR analysis.

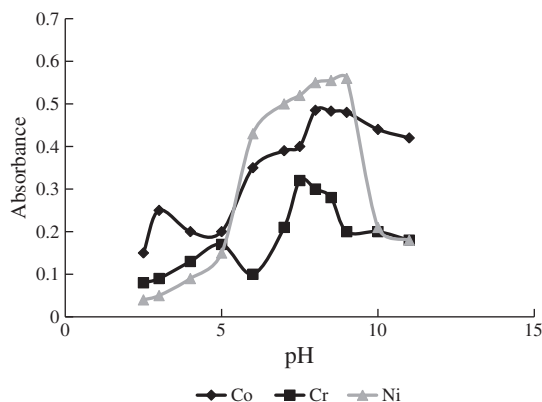| $\overline{\upsilon}$ (cm^{-1})	λ_{min} (cm^{-1})	λ_{max} (cm^{-1})
1559.3	1466.8	1699.1
1420.5	1394.7	1464.1
847.6	797.3	915.8
650.9	623.9	676.7

Fig. 3. Influence of the pH on the retention of Co, Cr and Ni.

Table 4
Factor levels in the screening and CCD designs.

Factor	Levels		
	−1	0	+1
Experimental domain for the full factorial design			
A: Molar relation Si/C	1.00	1.75	2.50
B: Infiltration temperature (ºC)	1410	1500	1600
C: Infiltration time (h)	0.50	2.25	4.00
Experimental domain for the Plackett–Burman experiment			
D: Volume of HFc (ml)	2	4	6
E: Volume of HNO_3c (ml)	2	4	6
F: Volume of H_2SO_4c (ml)	2	3	4
G: Microwave power (W)	500	950	1400
H: Digestion time (min)	10	35	60
I: ramp time (min)	2	6	10
Experimental domain for the CDC experiment[a]			
D	6	8	10
E	6	8	10
H	60	90	120

c = concentrated.

[a] Factors F, G and I were fixed at 4 ml, 1400 W and 2 min, respectively.

Table 5
Results for the determination of Ni, Cr and Co by FI-ETAAS.

Biomorphic samples	Element	Added($\mu g\, g^{-1}$)	Found ($\mu g\, g^{-1}$)	Recovery/%
Oak	Ni	–	571 ± 4	
		373	934 ± 9	97.3
		746	1299 ± 57	97.6
	Cr	–	108 ± 7	
		125	238 ± 18	104.0
		250	354 ± 17	98.4
	Co	–	15 ± 5	
		15	31.1 ± 0.6	107.3
		30	46 ± 4	103.3
Beech	Ni	–	74 ± 5	
		70	149 ± 2	107.1
		140	214 ± 5	100.0
	Cr	–	29 ± 1	
		38	65.7 ± 0.8	96.6
		76	106 ± 2	101.3
	Co	–	42 ± 8	
		32	74.1 ± 0.7	100.3
		64	104 ± 2	96.9
Eucalyptus	Ni	–	1202 ± 80	
		667	1839 ± 38	95.5
		1333	2537 ± 31	100.2
	Cr	–	327 ± 9	
		250	597 ± 30	108.0
		500	814 ± 11	97.4
	Co	–	91 ± 1	
		160	260 ± 9	105.6
		320	404 ± 32	97.8
Swedish pine	Ni	–	326 ± 12	
		200	537 ± 6	105.5
		400	716 ± 17	97.5
	Cr	–	53 ± 14	
		95	145 ± 7	96.8
		190	239 ± 8	97.9
	Co	–	9 ± 1	
		16	25 ± 2	100.0
		32	41.5 ± 0.4	101.6

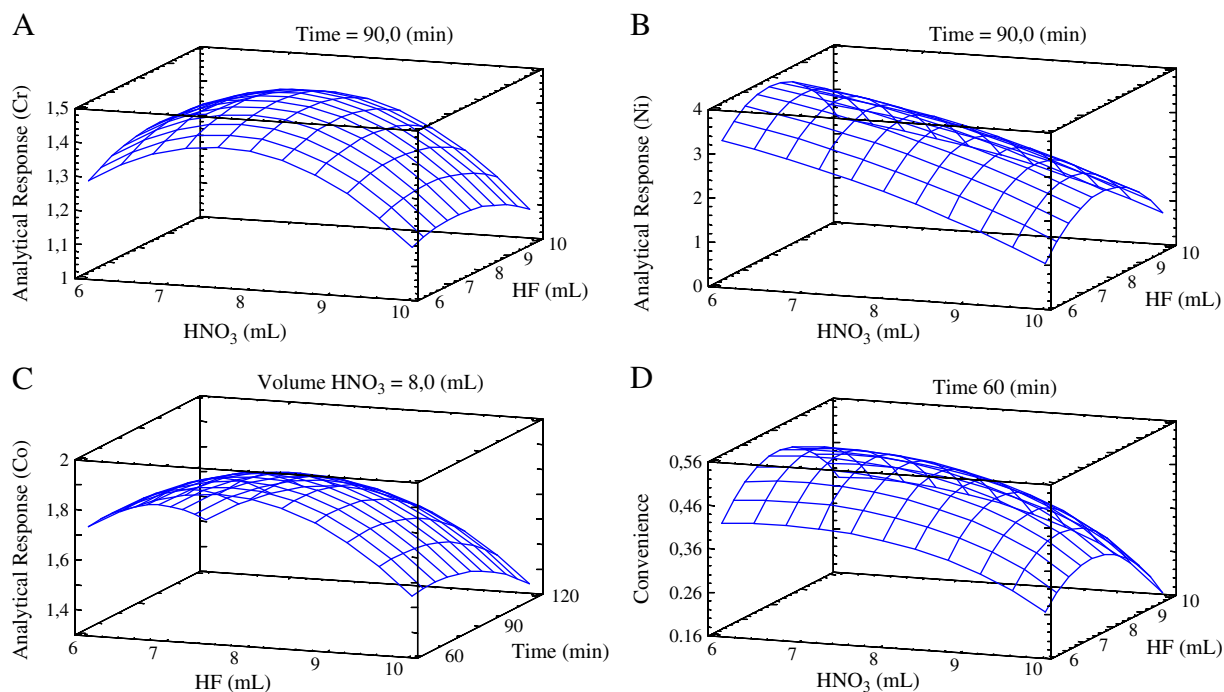Mean ± S.D. for three separate determinations.

significant level. According to ANOVA data, A, B, D and E were the important factors for the digestion procedure, with a positive effect. From this first experiment, one deduces the necessity of continuing the optimization. For this study, the choice of the values for the factors that were not statistically significant was carried out according to the sign of the estimated effect associated to it. Thus, factors C and F were fixed at 4 ml and 2 min, respectively. Also, factor D was kept constant at the maximum value of microwave oven (1400 W).

Once these factors have been fixed, a CCD involving 22 runs was then performed in order to obtain the optimum conditions with the three variables found to be potentially significant for this study. The experimental domain levels for CCD experiments appear in Table 4. Three dimensional representations keeping one of the variables at the

Fig. 4. Response surfaces obtained for the central composite design by plotting, (A) and (B) volume of concentrated HF against volume of concentrated HNO_3 for Cr and Ni, respectively; (C) digestion time against HF volume for Co; (D) simultaneous optimization of the Cr, Ni and Co responses.

central point value are presented in Fig. 4. It was observed that at a constant time of 90 min better response for Cr was obtained when both factors A and B were in the medium of the range (Fig. 4A). For a digestion time of 90 min higher responses were obtained for Ni at low factor B values (Fig. 4B). Finally, if factor B was fixed to 8 ml, higher responses were obtained for Co when both factors A and E were in the medium of the range (Fig. 4C). These data indicate that interactions usually occur between principal factors. This means that the response surfaces in the factorial space are curved in the domain of the experimental design. On the other hand, the most combinations of the three factors for simultaneous optimization of the three responses (Fig. 2D) were: A = 7.8 ml, B = 6.6 ml and E = 60 min, when factors C, D and F were fixed at 4 ml, 1400 W and 2 min, respectively. These digestion conditions were chosen for latter experiments. The objective was the obtaining of common conditions to three analytes, with the purpose of simplifying the process and avoiding a preparation by triplicate of the samples.

3.4. Analysis of biomorphic ceramics

The content of metal species in the samples was evaluated under the aforementioned instrumental conditions (Table 1). For the determination, 10 mg of powdered samples were weighed exactly, added to the digestion vessel and the recommended digestion procedure was applied for each sample. After digestion, the samples were prepared as described under on-line preconcentration/separation and determination procedure. The standard addition procedure was used in all cases. The results, as the average of three separate determinations, are given in Table 5. As there are no adequate certified reference materials available, for validation purposes, the metal ions were added to the powdered samples, then the samples were digested and analysed. The recoveries were found to be in the range of 95.5–108.0%.

The contained elements in the samples show a wide variability, presumably as a result of the different origin of the wood used in the preparation of the biomorphic materials.

4. Conclusions

The design of experiments has proved to be an excellent tool to optimize process. In this work as the synthesis as the dissolution of biomorphic SiC ceramic were optimized by this methodology. The factorial model used for optimization of the synthesis represents the behaviour of the dependent variable (yield of SiC) in a 96.8%. The considered factors, initial amount of Si, infiltration time and temperature produced positive effects on the SiC yield. Then, for a Si/C molar ratio 2.5, infiltration temperature 1600 °C and infiltration time 300 min, the SiC yield obtained was 90 ± 8%, very close to 100% of infiltration of the biocarbon template from beech.

The determination of metal traces in these ceramics can be achieved by the dissolution in acids under microwave irradiation, followed by the analysis of ETAAS. The method proposed in this paper is rapid, easy to use, automatic and selective with a good sensitivity for the determination of cobalt, nickel and chromium. The FI-ETAAS system has the advantage being able to be fully automated without complicated hardware and software; in fact modification of the software of the spectrometer and the use of additional computers were not necessary. On the other hand, dissolution under microwave irradiation shortens appreciably the time of the acid attack.

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