Microwave-induced combustion method for the determination of trace and ultratrace element impurities in graphite samples by ICP-OES and ICP-MS

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ABSTRACT

Graphite is extremely difficult to digest even using concentrated acids and quality control of impurities is critical for its industrial application. In this work, microwave-induced combustion is proposed for graphite digestion and further determination of Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V and Zn by inductively coupled plasma optical emission spectrometry (ICP OES). A relatively high graphite mass (400 mg) was completely burnt using 20 bar O_2 and HNO_3 (1–14.4 mol L^{-1}) as absorbing solution. A high digestion efficiency (>99%) was obtained with recoveries better than 95% for all analytes just using a solution as diluted as 4 mol L^{-1} HNO_3. Determination was also performed by inductively coupled plasma mass spectrometry (ICP-MS) with an agreement better than 97% with ICP OES results. Additionally, a microwave-assisted acid digestion/extraction method using concentrated HNO_3 and high-pressure system was performed and an agreement better than 95% was achieved in comparison to MIC results. Analysis of certified reference materials was also performed (agreement >95% to certified values). The proposed method allowed using diluted acids, resulting in digests fully compatible with multielemental analysis allowing lower blanks and better limits of quantification.

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1. Introduction

Graphite is a material with many applications in industrial processes and widely used for several applications [1]. Synthetic graphite has an important application in industry due to its peculiar properties, like high electrical and thermal conductivity, as well as lubricant action [2]. Some applications of graphite include alkaline batteries, electric conductors and industrial electrodes [2]. Furthermore, high purity graphite has been used as a moderator, reflector and fuel matrix in several types of nuclear reactors due to its inertness to irradiation and also chemical attack [3–7]. However, some contaminants can affect graphite properties even at trace levels (such as Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V and Zn) and the development of reliable methods for inorganic impurities determination is considered a key factor for its quality control [3].

The determination of elemental impurities in graphite is not a simple task, and the main problem is related to sample preparation step since graphite materials are extremely difficult to bring into solution in view of their stable structure [8]. Graphite is hardly digested by conventional wet digestion methods even using concentrated acids

combined with high temperature and pressure conditions [9,10]. As a consequence, a high volume of concentrated acids is required and final digests/extracts normally present high acid concentration, which cannot be supported by some analytical techniques such as inductively coupled plasma optical emission spectrometry (ICP OES) or inductively coupled plasma mass spectrometry (ICP-MS) [3,10,11]. In this sense, excessive acid concentration in digests makes necessary a dilution step that can avoid achieving suitable limits of detection (LOD) [11]. Alternatively, techniques allowing the direct determination of elements in solid samples, such as energy dispersive X-ray fluorescence (EDXRF), graphite furnace atomic absorption spectrometry (GF-AAS) [5,12], or electrothermal vaporization (ETV) coupled to ICP-based techniques, such as ICP OES or ICP-MS, can be used. [1,5,12] However, in these techniques, small amounts of sample are normally required that could affect the precision of measurements since samples could be not homogeneous [13].

Microwave-induced combustion (MIC) method allows burning organic samples in a quartz vessel pressurized with oxygen generally using diluted solutions for analytes absorption [14]. MIC has been applied for some organic matrices considered as hard to be digested by conventional acid digestion methods [15] such as coal [16], petroleum coke [17,18] and carbon nanotubes [19,20]. As organic matter is oxidized due to the action of oxygen present in gas phase, problems

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related to contamination and high blank values due to the use of concentrated reagents can be minimized. In this sense, as diluted absorbing solutions are used, lower LODs are normally obtained, also allowing the compatibility of digests with many techniques as, ion chromatography [17,21], potentiometry and especially ICP-based techniques [15,16,18,22,23]. Additionally, in order to assure that products will be completely absorbed in solution, it is possible to apply a reflux step after sample combustion improving analytes recovery [15]. In the same way, losses of analytes due to volatilization are minimized once the procedure is performed in a closed system. However, it is important to mention that the stable molecular structure of graphite makes difficult its combustion even using systems pressurized with oxygen.

By considering the lack of methods for graphite analysis, in this work, MIC was proposed for the decomposition of graphite samples and final digests were analyzed by ICP OES for the simultaneous determination of seventeen elemental impurities (Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V and Zn). The feasibility of analysis by ICP-MS was also evaluated for some elements. The concentration of absorbing solution was evaluated in order to obtain quantitative analyte recoveries. The maximum sample mass that can be burnt was studied taking into account the increase of pressure and also the efficiency of graphite decomposition, which was evaluated by the residual carbon content (RCC) in digests. In addition, a microwave-assisted acid digestion/extraction (MW-AD) and certified reference materials (BCR 40 and NIST 1632b) were used in order to check the accuracy of the proposed method. Furthermore, the possibility of using diluted solutions was discussed in order to reduce or eliminate the generation of laboratory effluents that are hazardous to human health or to environment.

2. Experimental

2.1. Instrumentation

A microwave oven (Synthos 3000, Anton Paar, Austria) equipped with high-pressure quartz vessels (80 mL, maximum pressure and temperature of 80 bar and 280 °C, respectively) was used for MIC and MW-AD digestion. Graphite samples were pressed as pellets (Specac, Orpington, United Kingdom), and introduced into vessels using a quartz holder. An inductively coupled plasma optical emission spectrometer (Optima 3000 DV, Perkin Elmer, EUA) was used for the determination of C (for RCC evaluation) and also Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V and Zn in digests. The determination of Cd, Co, Cr, Cu, Mn, Mo, Ni, Sr, V and Zn was also performed using an inductively coupled plasma mass spectrometer (Elan DRC II, PerkinElmer Sciex, Canada). Argon (99.999%, White Martins-Praxair, Brazil) was used for plasma generation for ICP OES and ICP-MS analysis. The operational conditions used for both ICP OES and ICP-MS determination of elements are described in Table 1.

Samples were weighed using an analytical balance (model AY 220, max. 220 g, 0.1 mg of resolution, Shimadzu, Japan). All statistical comparisons were performed using GraphPad InStat (GraphPad InStat Software Inc, Version 3.00, 1997). A significance level of $P > 0.05$ was selected for all comparisons.

2.2. Samples, reagents and standards

High purity graphite powder (particle size < 50 μm, 99.99%, Cat. nr. 104206, Merck, Darmstadt, Germany) was used for the evaluation of digestion efficiency by using MIC and MW-AD. After MIC method optimization, graphite samples used as electric contact and lubricant (purchased in a local market) were digested.

High purity water (18.2 MΩ cm) was used for preparation of all reagents and standard solutions. Nitric acid (65%, Merck) was previously purified using a sub-boiling system (Milestone, Model Duopur, Italy). Hydrogen peroxide (30%, Merck) was used without purification. Reference solutions for ICP OES and ICP-MS calibration were prepared by

Table 1
Operational conditions used for the determination of elemental impurities and C (for RCC evaluation) by ICP OES and ICP-MS.

Parameter	ICP OES	ICP-MS
RF power, W	1400	1500
Plasma gas flow rate, L min^{-1}	15.0	15.0
Auxiliary gas flow rate, L min^{-1}	1.2	1.2
Nebulizer gas flow rate, L min^{-1}	1.15	1.10
Spray chamber	Cyclonic	Cyclonic
Nebulizer	GenCone	Concentric
Observation view	Axial	–
Analyte	Emission line[a], nm	Isotope m/z
Ba	233.527 (II)	–
C	193.091 (I)	–
Ca	393.366 (II)	–
Cd	228.802 (I)	111
Co	228.616 (II)	59
Cr	267.716 (II)	53
Cu	324.752 (I)	65
Fe	238.204 (I)	–
K	766.490 (I)	–
Li	670.784 (I)	–
Mg	285.213 (I)	–
Mn	259.372 (II)	55
Mo	202.031 (II)	98
Na	589.592 (I)	–
Ni	231.604 (II)	60
Sr	407.771 (II)	88
V	290.880 (II)	51
Zn	213.857 (I)	66

[a] (I) atomic and (II) ionic emission lines.

dilution of multielement stock solution (SCP33MS, SCP Science, Canada, 10 mg L^{-1}) in 0.7 mol L^{-1} HNO$_3$. Absorbing solutions (1, 4, 7 and 14.4 mol L^{-1} HNO$_3$) for MIC digestion were prepared by dilution of concentrated HNO$_3$ in water. A solution of 6 mol L^{-1} NH$_4$NO$_3$ (Merck) was used as igniter for MIC method. Oxygen (99.6%, White Martins-Praxair) was used in MIC system.

Filter paper (15 mm of diameter, 12 mg, Black Ribbon Ashless, Schleicher and Schuell, Germany) was previously cleaned using 2.8 mol L^{-1} HNO$_3$ for 20 min in an ultrasonic bath, rinsed with water and dried in a class 100 laminar flow bench before use.

Certified reference materials (BCR 40, trace elements in coal, Brussels, Belgium and NIST 1632b, trace elements in coal, Gaithersburg, USA) were analyzed using the proposed MIC procedure.

2.3. Sample preparation procedures

For the proposed MIC method, graphite pellets with masses ranging from 50 to 500 mg were digested using 6 mL of absorbing solution (1, 4, 7 or 14.4 mol L^{-1} HNO$_3$). In order to assure a complete sample combustion and contrarily to previous works, two disks of filter paper were necessary to be placed on the quartz holder for helping sample ignition. Each vessel was pressurized with 20 bar oxygen, and microwave irradiation was performed using 1400 W during 5 min followed by a cooling step (0 W, 20 min). Final digests were made up with water to a final volume of 25 mL.

Graphite samples were extracted/decomposed by MW-AD in the same high-pressure closed vessels used for MIC. In this system, 6 mL of 14.4 mol L^{-1} HNO$_3$ and 2 mL of 30% H$_2$O$_2$ were used for the extraction/digestion of 250 mg of graphite. The operational conditions and the heating program were carried out according to recommendations of the manufacturer [24] as follows: i) 1400 W (10 min of ramp), ii) 1400 W for 40 min and iii) 0 W for 20 min (cooling). After cooling, extracts were made up with water to a final volume of 25 mL.

2.4. Evaluation of MIC digestion efficiency

In order to evaluate the digestion efficiency of MIC and MW-AD, the RCC determination in digests was performed using ICP OES as previously