



Microwave-induced combustion of high purity nuclear flexible graphite for the determination of potentially embrittling elements using atomic spectrometric techniques



Michele Stefani Peters Enders, Juliana Pinheiro de Souza, Paula Balestrin, Paola de Azevedo Mello, Fabio Andrei Duarte, Edson Irineu Muller *

Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

ARTICLE INFO

Article history:

Received 22 June 2015

Received in revised form 31 August 2015

Accepted 17 September 2015

Available online 25 September 2015

Keywords:

High purity nuclear flexible graphite

Embrittling elements

Microwave-induced combustion

Inductively coupled plasma optical emission spectrometry

Digestion

Elemental impurities

ABSTRACT

Microwave-induced combustion was evaluated for the digestion of high purity nuclear flexible graphite for further determination of potentially embrittling elements (Ag, As, Bi, Cd, Ga, Hg, In, Pb, Sb, Sn and Zn) using atomic spectrometric techniques. Flexible graphite is obtained by exfoliation process of conventional graphite using oxidant agents and subsequent fast heating at high temperatures. Thus, high chemical inertness for specific purposes is attained which causes inertness also to conventional digestion methods. Microwave-assisted digestion method using maximum temperature and pressure of 275 °C and 180 bar (UltraWave™ system) respectively, and dry ashing were also evaluated for flexible graphite digestion. However, insoluble residues in final digests and analyte losses were observed for those methods, respectively. For microwave-induced combustion method, the use of cellulose pellet (300 mg) as combustion aid allowed the efficient oxidation of 100 mg of flexible graphite. In order to assure the quantitative recovery of all analytes after microwave-induced combustion two absorbing solutions should be used: 4 mol L⁻¹ HNO₃ for Ag, As, Cd, Ga, Hg, In, Pb, and Zn and inversed *aqua regia* for Bi, Sb and Sn. As flexible graphite (or similar matrix) is not available as certified reference material, accuracy was evaluated using coal (NIST 1632c and BCR 40). For all elements, except for In (not informed in certified reference materials), significant differences were not observed by comparing the results obtained by microwave-induced combustion and certified values (*t* test, 95% confidence level). Limits of detection using inductively coupled plasma optical emission spectrometry and chemical vapor generation atomic absorption spectrometry (only for Hg) were lower than 12 mg kg⁻¹ and in compliance with the recommendation of General Electric for nonmetallic materials (the limit for each element is 200 mg kg⁻¹ and the sum of all embrittling elements should be lower than 500 mg kg⁻¹). Microwave-induced combustion method was suitable for quality control of high purity nuclear flexible graphite.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Flexible graphite (FG) is a flexible sheet produced from natural graphite by intercalation with sulfuric or nitric acid, followed by exfoliation by fast heating at high temperature (up to 1000 °C). Exfoliation process increases the resilience, impermeability to fluids and chemical inertness of FG in comparison to graphite used as raw material. Due to its specific characteristics, FG has been used as a non-metallic material in water-reactor nuclear power plant (WRNPP) applications [1–4].

The degradation of different materials used in WRNPP has been a frequent problem. One of these problems is the embrittlement process caused by metals in WRNPP operational conditions. Embrittlement is a loss of ductility of a material, making it brittle and can be caused by diffusion of atoms of metal, either solid or liquid into the WRNPP materials.

In this sense, elements such as Ag, As, Bi, Cd, Ga, Hg, In, Pb, Sb, Sn and Zn can promote embrittling process because the temperatures used in WRNPP are close to the temperatures that these elements can promote the embrittling effect [5–8].

In order to avoid problems in WRNPP the purity of FG materials regarding the potentially embrittling elements should be controlled. The contamination of embrittling elements present in FG can occur due to the presence of trace elements in raw materials (e.g. graphite and intercalate reagents) used during the production of FG. According to the recommendation of General Electric for nonmetallic materials, the maximum concentration of each potentially embrittling metal should be lower than 200 mg kg⁻¹ and the sum of all of these elements should be lower than 500 mg kg⁻¹ [8]. Despite the requirements for the determination of embrittling elements in this kind of material, works related to the determination of these elements in FG are scarce in literature, probably due to the refractory characteristics of this material to the conventional wet digestion methods. According to the literature, FG

* Corresponding author.

E-mail address: edson_muller@yahoo.com.br (E.I. Muller).

material is more refractory to oxidation process than common graphite probably due to the exfoliation process that increases the chemical inertness of this material [1,2]. Thus, conventional wet digestion methods, even using high temperature and pressure and combining strong oxidizing acids, can be ineffective.

Particularly in these cases and for organic refractory matrices, combustion methods are preferred allowing to obtain final digests with relatively low residual carbon content (RCC). Among the main methods used for the digestion of refractory organic samples include dry ashing and microwave-induced combustion (MIC). Dry ashing is a very simple method that allows the oxidation of relatively large sample mass of organic matrix (up to 10 g) with subsequent dissolution of resultant residues using diluted acids [9]. It is well reported in literature that losses of volatile elements (such as As, Cd, Pb and Hg) were significant for dry ashing digestion as well as contamination caused by the laboratory environment. In this sense, the heating program for dry ashing should be evaluated for each sample and additives can be added to the sample in order to minimize analyte losses [9,10].

MIC has been used for the digestion of several organic refractory matrices providing final digests with residual carbon content (RCC) lower than 1% [10–17]. Recently, MIC was used for the digestion of common graphite allowing the digestion of sample mass up to 400 mg [16]. In order to increase the sample mass or assure the efficient digestion of refractory organic samples or analyte release from matrix using MIC, some attempts have been carried out mixing easily combustible materials (e.g. cellulose) with these samples to provide enough energy to aid the combustion process [18]. Additionally, it is important to point out that the choice of absorbing solution for the determination of metals and metalloids by MIC depends on the characteristics and solubility of each element. Usually, quantitative recoveries for elements have been obtained using diluted acids (e.g. for metals) or alkaline solutions (e.g. for halogens). On the other hand, concentrated acids (HNO₃ and HCl) or a mixture of these acids is required in order to assure the quantitative recoveries for some applications [19].

In this work, MIC was evaluated for FG sample digestion for subsequent determination of potentially embrittling elements (Ag, As, Bi, Cd, Ga, Hg, In, Pb, Sb, Sn and Zn) using atomic spectrometric techniques. Some parameters of MIC method such as sample mass, use of cellulose as combustion aid, type and concentration of absorbing solution were evaluated to assure the quantitative recoveries of embrittling elements. Additionally, dry ashing and microwave-assisted digestion (MAD) were also used for FG digestion. Finally, accuracy of MIC was evaluated using certified reference materials (CRMs) of coal (NIST 1632c and BCR 40) once a CRM for FG is not commercially available.

2. Experimental

2.1. Reagents, solution and samples

Purified water (resistivity of 18.2 MΩ cm) was obtained using a Milli-Q system (Millipore, Bedford, USA) and it was used to prepare all solutions. Reagents were of analytical grade and acquired from Merck (Darmstadt, Germany). Nitric acid 65% has been purified by sub-boiling distillation system (Milestone, Sorisole, Italy). MIC digestions were carried out under oxygen pressure with purity better than 99.6% (White Martins, São Paulo, Brazil). Plasma-based instruments were operated using argon with purity higher than 99.998% (White Martins, São Paulo, Brazil). External calibration for the determination of Ag, As, Bi, Cd, Ga, Hg, In, Pb, Sb, Sn and Zn was carried out using suitable dilution of 1000 mg L⁻¹ standard solutions (Spex CertiPrep, Metuchen, USA). Four samples of flexible graphite sheet (named as FG I, FG II, FG III and FG IV) donated by two private companies were used in this work. Accuracy of MIC method was evaluated using CRMs with high carbon content matrices – NIST 1632c (National Institute of Standard and Technology, trace elements in coal) and BCR 40 (Community Bureau of Reference, trace elements in coal).

For recovery experiments, spiked samples were prepared by adding a known amount of a standard solution (the same that was used for calibration) containing all potentially embrittling elements, over the sample pellet before the MIC and dry ashing digestions. FG sample “IV” was arbitrarily chosen for these experiments and the results obtained by the analyte spike were used to calculate the recovery of all analytes.

2.2. Instrumentation

FG sheet samples were milled in a cryogenic mill (Spex CertiPrep, model 6750, Metuchen, USA) and this procedure was repeated until the whole sample showed particle size lower than 80 μm. An analytical balance (model AY 220, Shimadzu, São Paulo, Brazil) was used to weigh samples and reagents.

All embrittling elements (exception of Hg) were determined using an inductively coupled plasma optical emission spectrometer (Ciros CCD model, Spectro, Kleve, Germany) equipped with a Scott-type double pass spray chamber, a cross-flow nebulizer, a torch and a quartz injector. The operational conditions were summarized in Table 1. Determination of Hg was carried out using a homemade flow-injection (FI) system for chemical vapor generation (CVG) with detection by atomic absorption spectrometry (AAS). It consisted of a peristaltic pump (Ismatec, Zurich, Switzerland), an injection valve fitted with 100 μL sample loop and a U type gas-liquid separator. Mercury determination was carried out using an atomic absorption spectrometer (Vario 6 model, Analytik Jena, Jena, Germany) equipped with a heated quartz cell furnace (HS5, 100 mm length, 10 mm i.d.). A mercury hollow cathode lamp operated at 4.0 mA was used as a radiation source and a deuterium lamp was used for background correction. The wavelength was set at 253.7 nm and the spectral band pass at 0.5 nm. All measurements were performed in integrated absorbance (peak area) [20].

Some embrittling elements were also determined in CRMs using inductively coupled plasma mass spectrometry (ICP-MS) because their concentrations were lower than the LOD provided by ICP-OES (Table 1). Determination was carried out using inductively coupled plasma mass spectrometer (Elan DRC II model, Perkin Elmer).

Digestion of FG samples using MIC was performed using a Multiwave 3000 microwave sample preparation system (Anton

Table 1
Operational parameters for analyte determination by ICP-OES and ICP-MS.

Parameter	ICP-OES	ICP-MS
RF power (W)	1600	1400
Plasma gas flow rate (L min ⁻¹)	14	15
Auxiliary gas flow rate (L min ⁻¹)	1.00	1.20
Nebulizer gas flow rate (L min ⁻¹)	0.80	1.09
Spray chamber	Scott-type double pass	Cyclonic
Nebulizer	Cross-flow	Concentric
Wavelength (nm)	Ag 328.068 As 188.979 Bi 223.061 Cd 228.802 Ga 417.206 In 230.606 Pb 220.353 Sb 206.836 Sn 189.927 Zn 206.200	–
Dwell time (ms)	–	50
Sweeps/reading	–	5
Readings/replicate	–	3
Replicates	–	3
Data collection mode	–	Peak hopping
Sampler and skimmer cones	–	Pt
Isotopes (m/z)	–	¹⁰⁷ Ag ²⁰⁹ Bi ¹¹¹ Cd ⁷¹ Ga ¹²¹ Sb ¹¹⁸ Sn

Download English Version:

<https://daneshyari.com/en/article/7642194>

Download Persian Version:

<https://daneshyari.com/article/7642194>

[Daneshyari.com](https://daneshyari.com)