



# An evaluation of microwave-assisted fusion and microwave-assisted acid digestion methods for determining elemental impurities in carbon nanostructures using inductively coupled plasma optical emission spectrometry



Shashikant P. Patole<sup>a,\*</sup>, Filipa Simões<sup>a</sup>, Tahir F. Yapici<sup>b</sup>, Bashir H. Warsama<sup>b</sup>, Dalaver H. Anjum<sup>c</sup>, Pedro M.F.J. Costa<sup>a</sup>

<sup>a</sup> Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

<sup>b</sup> Analytical Core Laboratory, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

<sup>c</sup> Advanced Imaging and Characterization Laboratory, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

## ARTICLE INFO

### Article history:

Received 24 June 2015

Received in revised form

18 October 2015

Accepted 20 October 2015

Available online 21 October 2015

### Keywords:

Metrology

Carbon nanotubes

Graphene nanoplatelets

Microwave-assisted acid digestion

Microwave-assisted fusion

Inductively coupled plasma optical emission spectrometry

## ABSTRACT

It is common for as-prepared carbon nanotube (CNT) and graphene samples to contain remnants of the transition metals used to catalyze their growth; contamination may also leave other trace elemental impurities in the samples. Although a full quantification of impurities in as-prepared samples of carbon nanostructures is difficult, particularly when trace elements are intercalated or encapsulated within a protective layer of graphitic carbon, reliable information is essential for reasons such as quantifying the adulteration of physico-chemical properties of the materials and for evaluating environmental issues. Here, we introduce a microwave-based fusion method to degrade single- and double-walled CNTs and graphene nanoplatelets into a fusion flux thereby thoroughly leaching all metallic impurities. Subsequent dissolution of the fusion product in diluted hydrochloric and nitric acid allowed us to identify their trace elemental impurities using inductively coupled plasma optical emission spectrometry. Comparisons of the results from the proposed microwave-assisted fusion method against those of a more classical microwave-assisted acid digestion approach suggest complementarity between the two that ultimately could lead to a more reliable and less costly determination of trace elemental impurities in carbon nanostructured materials.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbon nanotubes (CNTs) and graphene belong to a special class of graphitic materials that offer a diversity of applications because of their unique physical and chemical properties [1]. As it is known, most growth methods for CNTs and graphene formation rely on the use of transition metal catalysts [2–7]. In the process of synthesizing these nanostructures, it is highly probable that elements other than C will be present in the final product. Furthermore, mass production of graphene platelets via exfoliation methods depends on the use of graphite as a starting material. The latter is commonly obtained from mines and invariably contains various impurities such as intercalated elements [8]. Several approaches have been developed to remove these contaminants from carbon nanostructures [9–15].

\* Corresponding author.

E-mail address: [Shashikant.Patole@kaust.edu.sa](mailto:Shashikant.Patole@kaust.edu.sa) (S.P. Patole).

Central to the effort of purifying CNT and graphene materials is the capability to accurately quantify their impurities [16,17]. Therefore, there has been much effort lately in developing metrology and standardization methods for carbon nanostructure analysis in order to implement accurate quality control checks. These are of the utmost relevance for research-grade samples just as for industrially-produced batches [17–23]. Unfortunately, there is a growing crisis in the field owing to the lack of affordable and sufficiently sensitive and selective analytical methods [9–15]. Commonly available characterization tools include energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), Raman spectroscopy and thermogravimetric analysis (TGA) [23–27]. However, EDX, SEM, TEM and EELS are too localized, limiting the global information about the sample, XPS and XRF are surface-limited methods and Raman spectroscopy and TGA are not suitable for providing an accurate quantitative analysis of trace elements. Other less common tools include

nuclear magnetic resonance methods [28] and terahertz spectroscopy [29], magnetic susceptibility and electron paramagnetic resonance for finding trace levels of magnetic impurities in CNTs [30], and ion-beam analysis (IBA) and neutron activation analysis (NAA) for directly analyzing solid samples. The NAA has been proposed as a “gold-standard” for the determination of trace elemental impurities in CNTs [21,31], while showing high sensitivity and selectivity for a range of elements. However, both IBA and NAA require expensive and sophisticated equipment, hence outside the realm of routine analysis.

Inductively coupled plasma optical emission (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are widely available tools in research and industrial laboratories, offering exceptional sensitivity and accuracy along with multi-element measurement capabilities [32]. The key issue in these two techniques is the solid sample pretreatment method as it is necessary to fully dissolve the sample (including any trace impurity) and obtain a transparent homogeneous aqueous solution. The challenge concerning the determination of trace impurities in CNTs and graphene is precisely the sample preparation step for plasma based techniques since these materials are extremely difficult to bring into solution [17–20]. In 2008, Ge et al. used NAA and ICP-MS to determine metal concentrations in CNTs [18]. Different sample pretreatment methods, involving dry ashing coupled with acid extraction, wet digestion and a combination of dry ashing/acid digestion, were used prior to ICP-MS analysis. In the absence of a reference material for CNTs, the NAA results were used as the best estimate of the true value of metallic impurities. In a related study, Yang et al. used water extraction, dilute acid extraction and microwave-assisted acid digestion to leach metal impurities from CNTs prior to ICP-OES and ICP-MS measurements [20]. The authors found that microwave-assisted acid digestion followed by ICP-OES analysis produced results closer to those obtained by NAA than to those obtained by ICP-MS. Furthermore, it was observed that ICP-MS mainly suffers from nonspectral interference induced by carbon residues in the sample solution. Truly, in the absence of a standard, it is difficult to trust the results by ICP techniques only. The reason is that the final aqueous solution generally contains the undissolved graphitic carbon in suspension, forming an inhomogeneous mixture. Filtering the solution can get rid of the particulates but adds further ambiguity in the final results (the filtered residual may contain elemental impurities intercalated in or encapsulated by undissolved graphitic carbon). Ayouni-De-rouiche et al. used the UltraWAVE digestion system, a modified version of the microwave-assisted acid digestion system, to obtain clear solutions of double-walled CNTs (DWCNTs) [19]. Thereafter, ICP-OES was employed to quantify the Mo and Co residuals of the growth catalyst, which the authors claim were completely dissolved. Recently, Grinberg et al. [33] applied several laborious matrix destruction procedures, including a multi-step microwave-assisted acid digestion, dry ashing at 450 °C and microwave-induced combustion with oxygen, to determine trace metal impurities in single-walled CNTs (SWCNTs) using ICP-MS. The results showed that the multi-step microwave-assisted acid digestion was the most reliable technique for recovering the analyte, although Cr content remained biased towards low values, likely due to the formation of a Cr refractory carbide.

Here, we propose the complementary approaches of microwave-assisted fusion and microwave-assisted acid digestion to prepare samples for ICP-OES. We test and discuss the potential of each method to leach trace elemental impurities from commercially available SWCNTs, DWCNTs and graphene nanoplatelets.

## 2. Experimental

### 2.1. Materials and reagents

SWCNTs and graphene nanoplatelets were purchased from STREM Chemicals, Newburyport MA, US. DWCNTs were purchased from Tokyo Chemical Industries Co. Ltd. Tokyo, Japan. As per the vendor's specifications, the SWCNTs sample contained > 90 wt% of 1–2 nm in diameter and 5–30 μm in length SWCNTs. The DWCNTs sample contained > 50 wt% of < 5 nm in diameter and 5–15 μm in length DWCNTs; the remainder was MWCNTs and other by-products. Graphene nanoplatelets were 6–8 nm thick and 15 μm wide with a surface area of 300 m<sup>2</sup>/g. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, for trace analysis, ≥ 99.9999%), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, for trace analysis, ≥ 99.995%), nitric acid (HNO<sub>3</sub>, trace metal grade, 70%), hydrochloric acid (HCl, trace metal grade, 34–37%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, trace metal grade, 30–32%), methanol and isopropyl alcohol were purchased from Sigma Aldrich. High-purity deionized water (DIW) with 18 MΩ cm resistivity was obtained from a Milli-Q water purification system (Millipore, UK). Single-element stock standard solutions were purchased from SCP Science, Quebec, Canada and Inorganic Venture, VA, USA. Custom-grade multi-element solution was supplied by Perkin Elmer Pure Plus.

### 2.2. Physical characterizations

SWCNTs, DWCNTs and graphene nanoplatelet sample morphology was observed using SEM (FEI Nova Nano 630) and TEM (FEI Titan G<sup>2</sup> 80–300 CT). For SEM observations, powder samples were either attached to the aluminum stub using double-sided carbon tape or liquid-dispersed samples were drop coated onto the stub. SEM images of as-received samples are provided in the [Supplementary information \(SI\)](#). For TEM observations, a small amount of each sample was dispersed in isopropyl alcohol with the help of tip sonication (750 W, 60% amplitude, 2/1 s on/off ratio pulse, total time 5–10 min). The well-dispersed liquid suspension was then drop coated onto the TEM grid (holey carbon on copper grid with 300 mesh from Electron Microscopy Sciences) and used for further analysis. TEM images of as-received samples are provided in the [SI](#). For the TEM of microwave-assisted acid digested samples, a residual was collected using a dropper and diluted in isopropyl alcohol. The diluted solution was then drop coated onto the TEM grid. For Raman analysis, as-received powdered samples were squeezed between two glass slides. These samples were analyzed by Raman spectrometer (Horiba Aramis) with excitation wavelength 473 nm. Raman analysis of as-received samples are provided in the [SI](#). Thermal analysis of samples was performed using TGA (Netzsch TG 209 F1 Iris) from 25 to 1000 °C in a dry air atmosphere (around 21% oxygen) with a flow rate of 25 sccm (sccm: standard cubic centimeters per minute). Plots are provided in the [SI](#).

### 2.3. Microwave system

The microwave-assisted digestion system used for the fusion and acid digestion of materials was an ETHOS 1-Advanced Microwave Digestion Labstation (Milestone S.r.l. Italy) with user-selectable output power (0–1500 W with 1 W increment). In general, the microwave-assisted digestion system can be used for either acid digestion or fusion of samples, depending on the accessories. Microwave-assisted acid digestion of samples can be performed using a polypropylene rotor equipped with 10 segments with 100 mL capacity Teflon vessels. Inside the vessels, the reaction temperature can be elevated up to 300 °C and directly monitored by an automatic temperature controller. Alternatively, microwave-

Download English Version:

<https://daneshyari.com/en/article/1243763>

Download Persian Version:

<https://daneshyari.com/article/1243763>

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