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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

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ABSTRACT

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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.

Keywords

Metrology; Carbon nanotubes; Graphene nanoplatelets; Microwave-assisted acid digestion; Microwave-assisted fusion; Inductively coupled plasma optical emission spectrometry

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, release through 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].

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-limiting 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-Derouiche 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^2/g . Sodium carbonate (Na_2CO_3 , for trace analysis, $\geq 99.9999\%$), potassium carbonate (K_2CO_3 , for trace analysis, $\geq 99.995\%$), nitric acid (HNO_3 , trace metal grade, 70%), hydrochloric acid (HCl , trace metal grade, 34-37%), hydrogen peroxide (H_2O_2 , trace metal grade, 30-32%), methanol and isopropyl alcohol were purchased from Sigma Aldrich. High-purity deionized water (DIW) with 18 $\text{M}\Omega\cdot\text{cm}$ 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 G² 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 watt, 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-assisted fusion of the samples was performed by replacing the polypropylene rotor with a muffle furnace bearing a rotating carousel. This accommodates up to four silicon carbide crucibles, which contain a quartz fiber insert and the actual fusion crucible made of zirconium. An external contact-less infrared

temperature sensor enables precise temperature control for all crucibles. Samples can be heated up to 1000 °C by employing user-defined programs.

2.4. *Microwave-assisted fusion method*

The experimental flow chart for sample preparation is shown in Fig. 1. Approximately 30 mg of graphene, SWCNTs or DWCNTs were weighed (to an accuracy of 1 µg) using an analytical balance. Na₂CO₃ and K₂CO₃ were combined to create a flux (300 mg of each). For reference, a blank flux was placed in a zirconium crucible. Three other containers were used bearing a mixture of flux and SWCNTs, DWCNTs or graphene. Prior to use, the zirconium crucibles were cleaned with hot concentrated HNO₃ (washed for several hours) followed by rinsing with DIW. In a typical experiment, fluxes were heated to 1000 °C at 1500 W within 40 min. A dwell step at this temperature was performed for 20 min. After completing the fusion step, the furnace was allowed to cool down to a moderate temperature so that the crucibles could be removed from the furnace and cooled to room temperature on an insulating platform inside a fume hood. Next, 7.5 mL of HNO₃ and 7.5 mL of HCl were added stepwise to each of the crucibles to entirely dissolve the fused materials. Finally, the obtained solutions were transferred into 50 mL vials and diluted using DIW to bring the final volume to 25 mL.

Fig. 1.

2.5. *Microwave-assisted acid digestion method*

The experimental flow chart for sample preparation is shown in Fig. 1. Approximately 30 mg of SWCNTs, DWCNTs or graphene were weighed and transferred into Teflon vessels. Prior

to use, vessels were cleaned with hot concentrated HNO_3 (washed for several hours) followed by rinsing with DIW. Approximately 7 mL of HNO_3 and 1 mL of H_2O_2 were added to the samples. Vessels were then fitted into the segments of the polypropylene rotor. The samples were microwave-heated to 220 °C within 10 min (at 300 W) and dwelled for 20 min. Next, the vessels were cooled to room temperature and individually transferred to a fume hood. The acid-digested samples were transferred into 50 mL vials and further diluted to a 25 mL volume using DIW.

2.6. ICP–OES analysis

An ICP–OES Varian 720-ES spectrometer equipped with a dual detector assembly that covered a wavelength range from 165 to 782 nm was used to quantify the elements. The flow rate for the plasma and auxiliary Ar gas were 16.5 L min⁻¹ and 1.5 L min⁻¹, respectively. The nebulizer Ar gas flow rate was 0.7 L min⁻¹. The forward RF power was 1.2 kW. The sample uptake rate, rinse time, pump rate, integration time and replicate were 1 mL min⁻¹, 35 s, 15 rpm, 30 s and 3, respectively. The diluted microwave-assisted fusion and microwave-assisted acid digested samples were screened for the presence of elements using ICP–OES. From the 40 elements scanned, only a few were found in measurable concentrations above the method's detection limit. To analyze the fusion samples, a reference flux was used to establish baseline concentrations of the elements. We followed Method 200.7 from the US Environmental Protection Agency, which requires that analytical errors should not exceed 5–10% for most quality controls [34]. Quality control for elemental analyses included repeated injections and periodic analysis (two in every 2 h operation of the equipment) of a Certified Reference Standard (CRS), NIST 1643d. The samples were re-run if the analyzed value of the CRS differed from its certified value by >10%. The relative standard deviation of four replicate determinations was typically ≤5%. Calibration solutions were prepared from single-element solutions. Stock standard solutions of Al, B, Co, Fe, Mo, Ni and S at a concentration of 1000 mg L⁻¹ were used to prepare a working calibration standard for ICP–OES in the range of 1, 10 and 100 mg L⁻¹. Check

standards were prepared from a custom-grade multi-element solution. The calibration blank was prepared from DIW with 1% v/v HNO₃.

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3. Results

3.1. Microwave-assisted fusion method

Fig. 2.

Figure 2A shows photographs of Zr crucibles containing either the reference flux or a powder blend of flux with SWCNTs before and after microwave-assisted fusion. Microwave-assisted fusion transformed both the flux alone and the blend into white, glassy melts. The melting points of Na_2CO_3 and K_2CO_3 are 851 °C and 891 °C, respectively, but mixing them in a 1:1 ratio forms a eutectic mixture that melts at approximately 710 °C (for the corresponding phase diagram refer to the SI). Consequently, at 1000 °C, the reference flux had completely melted. As Na_2CO_3 and K_2CO_3 approach 1000 °C, they begin to decompose [35] to form Na_2O and K_2O , liberating CO_2 gas, as shown in the following reaction:

After cooling, the resultant products, Na_2O and K_2O , solidify into a water-soluble, milky glass block. The addition of water into the flux results in the formation of NaOH and KOH as per the following reaction:

Knowing that the oxidation temperature of the as-received SWCNTs in air is below 680 °C (see Table 1), exposure to the 1000 °C carbonate melt was expected to cause a complete disintegration of the nanotubes. The CO₂ gas, liberated from the flux, oxidizes the SWCNTs by the following reaction:

The remainders, which in the TGA amount to 8.74 wt%, could be assigned to ash and metal impurities (Table 1) and explain the greyish coloring to the glass that forms upon cooling, as observed in Fig. 2A. Similarly, DWCNTs and graphene samples combust completely at 1000 °C leaving behind 10.75 wt% and 5.34 wt% of residuals, respectively (Table 1). Microwave-assisted fusion of these flux mixtures also resulted in a greyish coloration (not shown). Note that all solidified fluxes fully dissolved in water; however, it takes comparatively longer for them to dissolve in DIW than in the mixture of HNO₃ and HCl. Dissolution in the acid medium produced transparent solutions (Fig. 2B) that showed no evidence of agglomerated carbon particles, suggesting the complete digestion of SWCNTs, DWCNTs and graphene.

Table 1.

3.2. Microwave-assisted acid digestion method

In contrast, the microwave-assisted acid digestion approach was unable to assimilate the SWCNTs, DWCNTs and graphene samples despite the use of extreme conditions such as concentrated HNO_3 and H_2O_2 at 220°C . In microwave-assisted acid digestion of C, the following oxidation reaction is expected:

As seen from the photographs (Fig. 2b), the product of the acid digestion is an unstable suspension indicating the presence of carbon particulates. Within a few hours, a black sediment settled at the bottom of the vials, which is predicted to contain transition metals encapsulated in carbon onions, known to be notoriously difficult to eliminate, along with other impurities that are protected by undigested graphitic carbon [36]. In a previous study, Yang et al. observed similar sedimentation in SWCNTs and MWCNTs samples from microwave-assisted acid digestion. Although they used filter paper to remove the sedimentation from the aqueous solution prior to ICP–OES analysis [20], undigested CNTs remained in the aqueous solution rendering it unsuitable for ICP–OES elemental quantification.

3.3. ICP–OES

Results of the ICP–OES are shown in Table 2. The mean concentration ($\mu\text{g g}^{-1}$) and the percent relative standard deviation (%RSTD) were calculated from four sample aliquots. The full list of elements scanned and the respective wavelengths of atomic emission are presented in the SI.

Table 2.**3.3.1. SWCNT samples**

In SWCNT fusion samples, Co, Mo and Fe were the most dominant elements at 25110, 9650 and 2360 $\mu\text{g g}^{-1}$, respectively; these samples also contained $< 200 \mu\text{g g}^{-1}$ of Al, B and S. Similar trends were apparent among the analogous acid-digested samples with concentrations of Co, Mo and Fe of 48250, 11620 and 5020 $\mu\text{g g}^{-1}$, respectively; these samples also contained $< 430 \mu\text{g g}^{-1}$ of Al, B, Ni and S. Thus, we observed the following main difference in SWCNT samples:

- 1) Al, B, Co, Fe, Mo, and S are detected in larger quantities in the acid-digested samples.
- 2) Ni was detected in the acid digested but not in the fusion samples.

The highest %RSTD were for S (at 23%) in the fusion samples and Ni (10.5%) for the acid-digested samples.

3.3.2. DWCNT samples

DWCNT samples followed a different trend than did SWCNT samples. Using microwave-assisted fusion, the most abundant elements were Co, Mo and Fe at 31290, 9830 and 3100 $\mu\text{g g}^{-1}$, respectively. In the microwave-assisted acid-digested samples, Mo, Fe and Co were present at 2940, 2700 and 610 $\mu\text{g g}^{-1}$, respectively. Thus, we observed the following main differences in DWCNT samples:

- 1) Al, B and S were detected in larger quantities with acid-digested samples.

2) Co, Fe and Mo were detected in larger quantities in fusion samples.

3) Ni was detected in the acid digested but not in the fusion samples.

Similar to the SWCNT samples, the highest %RSTD were for S (24%) in the fusion samples and Ni (14.1%) for the acid-digested samples.

3.3.3. *Graphene nanoplatelet samples*

In graphene samples, S was present in the highest concentration for both fusion ($6880 \mu\text{g g}^{-1}$) and acid-digested ($6250 \mu\text{g g}^{-1}$) solutions. Other prominent elements in the fusion samples were Co ($6700 \mu\text{g g}^{-1}$) and Fe ($880 \mu\text{g g}^{-1}$). In acid-digested samples, the amount of Fe and Al was 1940 and $450 \mu\text{g g}^{-1}$, respectively. Thus, we observed the following main differences in graphene samples:

1) Al, B, Fe, and Ni were detected in larger quantities with acid-digested samples.

2) Mo, Co and S were detected in larger quantities in the fusion samples.

3) Co was detected in the fusion but not in the acid-digested samples.

The highest inhomogeneity was measured for Mo at 12.4% and 18.4% %RSTD in the fusion samples and acid-digested samples, respectively.

3.4. *Post-microwave product analysis*

To determine the source of the discrepancy between the results from the ICP-OES between fusion and acid-digested samples, we collected and characterized the sediments

obtained from the latter. Figure 3 shows high-resolution TEM images of SWCNT (Fig. 3A), DWCNT (Fig. 3B) and graphene nanoplatelet (Fig. 3C) samples subjected to the microwave-assisted acid-digested treatment. Retention of the graphitic structure of CNTs and graphene is visible. It is evident from the considerable damage to SWCNTs compared to DWCNTs and graphene nanoplatelets that the harsh acidic environment easily oxidized the single graphitic shell at many locations.

Fig. 3.

Bundles of DWCNTs are also present in the acid-digested sediments (Fig. 3B). Compared to the as-received material, the microwave-assisted acid-digested DWCNTs show an absence of by-product particles, implying that they have leached into the aqueous solution. As expected, only the outer layers of CNTs were damaged while the inner layers remained intact. In addition, isolated DWCNTs were more severely damaged than were bundles of DWCNTs (SI). In graphene nanoplatelet samples, only the outer layer appears damaged while inner multilayered stacks appear to have been unaffected by the acid digestion (Fig. 3C); when there were only a few layers of graphene, flakes were severely damaged (SI).

4. Discussion

Some of the results on the concentration levels of elements extracted from the microwave-assisted fusion and digestion solutions were conflicting. As it is often the case for vestigial contaminants, impurities may present themselves as sub-nm-sized clusters, isolated atoms or even chemically bonded cations. Their distribution over the as-prepared materials is unlikely to be homogeneous, rendering a localized analysis (e.g., by high-resolution TEM)

challenging if not unreliable. On the other hand, ICP–OES is a non-spatially localized analytical technique that is more suitable for evaluating trace elements from entire samples.

Here, impurities within the carbon nanostructure samples can be defined as the non-C elements. These can be found as aggregates or atoms and may be chemically (e.g., via covalent bonds) or physically (e.g., via van der Waals interactions) attached to the carbon nanostructures. For simplicity, we can categorize the impurities according to their location within the nanostructures as shallow, intermediate or deep impurities (Fig. 4). Shallow impurities are found on the outside of the carbon nanostructures (e.g., decorating the outer graphene layer), intermediate impurities are covered by a single layer of graphene (e.g., aggregates within SWCNTs) and deep impurities are covered by more than one graphene shell (e.g., encapsulated DWCNTs or carbon onions, intercalated in multilayer graphene or bundle interstitials).

Fig. 4.

A few assumptions are necessary to interpret results from ICP–OES:

- 1) the acid mix must come into direct contact with the impurity,
- 2) shallow impurities are easy to leach as they can come into direct contact with the acid,
- 3) deep impurities are difficult to leach as they are shielded by more than one graphene layer and
- 4) intermediate impurities are easier to leach than deep impurities as they are only shielded by a single graphene layer that can be damaged by the acid mix via oxidation.

In this scenario, microwave-assisted fusion and acid digestion act differently to extract trace impurities from SWCNTs, DWCNTs and graphene nanoplatelets. Despite possible disparities in the interactions between impurities and carbon, shallow and intermediate impurities

can be completely leached by either method; however, deep impurities can only be entirely extracted through the action of microwave-assisted fusion as this promotes the full disintegration of the protective graphitic carbon. This is corroborated by our analysis of the sediments originating from the microwave-assisted acid-digested aqueous solutions, in which samples had an abundance of the original carbon nanostructures. At this stage, we propose that the results from ICP-OES of microwave-assisted fusion and microwave-assisted acid-digested samples are complementary in their analysis of trace elements present in carbon nanostructures. Although microwave-assisted acid digestion is suitable for SWCNTs and single-layer graphene, it is less suitable for use with DWCNTs, MWCNTs, few-layer graphene or multilayered graphene. Meanwhile, microwave-assisted fusion is suitable for DWCNTs, MWCNTs, few-layer graphene and multilayered graphene. In the absence of a certified reference value, the highest detected elemental concentration (from a comparative digestion vs. fusion approach) should be interpreted as the most reliable figure for a specific trace element.

5. Conclusions

We have described a novel method of preparing aqueous solutions of carbon nanostructures in preparation for studying their elemental impurity levels using ICP-OES. The microwave-assisted fusion procedure capably disintegrated SWCNTs, DWCNTs and graphene nanoplatelets, which, upon dissolution of the flux in an acidic medium led to a homogenous, transparent solution. In contrast, the classical acid digestion method was incapable of assimilating graphitic carbon, invariably resulting in an unstable suspension. Nevertheless, results from both methods were complementary. We believe that the proposed fusion approach has the potential to facilitate the chemical analysis of carbon nanostructures by ICP-OES and, ultimately, the field of metrology of carbon materials.

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Figure captions

Fig. 1. Experimental flow chart showing the sample preparation steps in microwave-assisted fusion and microwave-assisted acid digestion methods prior to ICP-OES analysis.

Fig. 2. Photographs showing (A) zirconium crucibles containing a ‘reference flux’ of Na_2CO_3 and K_2CO_3 or a blend of the reference flux with SWCNTs before and after microwave-assisted fusion; (B) the appearance of the final aqueous solutions containing dissolved samples from microwave-assisted fusion and microwave-assisted acid-digestion of SWCNTs, DWCNTs and graphene nanoplatelets.

Fig. 3. TEM images showing the morphology of (A) SWCNT, (B) DWCNT and (C) graphene nanoplatelet samples after microwave-assisted acid digestion. The red circles show damaged sections of the graphitic lattice. Additional TEM images for these samples are provided in the SI.

Fig. 4. Possible locations of impurities in a SWCNT, a DWCNT, a CNT bundle, a carbon onion, multilayered graphene and single-layer graphene based on accessibility of the analyte for leaching in microwave-assisted acid digestion.

Highlights

Comparison of microwave-assisted fusion and acid digestions for carbon materials.

Full digestion of various carbon nanostructures for identical fusion conditions.

ICP—OES analysis suggests complementarity of fusion and acid digestions.

Table 1.

TGA analysis of as-received SWCNTs, DWCNTs and graphene nanoplatelets. Samples were heated in air (21% oxygen) at the rate of 5 °C min⁻¹ (TGA data in SI). The total mass change and residual mass were obtained at 1000 °C. The inflection temperature was obtained from the corresponding DTA curves.

Sample	Initial mass (mg)	Mass change (%)	Residual mass (%)	Inflection temperature (°C)
SWCNTs	2.579	91.26	8.74	680
DWCNTs	3.955	89.25	10.75	683
Graphene nanoplatelets	3.245	94.66	5.34	859

Table 2.

ICP-OES data showing mean concentrations (in $\mu\text{g g}^{-1}$) and %RSTD of impurity elements in SWCNT, DWCNT and graphene nanoplatelet solutions prepared using microwave-assisted fusion and microwave-assisted acid digestion methods. Each mean concentration was calculated from four aliquots.

Elements	SWCNTs				DWCNTs				Graphene nanoplatelets			
	Fusion		Digestion		Fusion		Digestion		Fusion		Digestion	
	($\mu\text{g g}^{-1}$)	(%RSTD)	($\mu\text{g g}^{-1}$)	(%RSTD)	($\mu\text{g g}^{-1}$)	(%RSTD)	($\mu\text{g g}^{-1}$)	(%RSTD)	($\mu\text{g g}^{-1}$)	(%RSTD)	($\mu\text{g g}^{-1}$)	(%RSTD)
Al	38	3.8	430	5	2	2.9	550	6	50	3.1	450	1.7
B	57	7.4	160	3.5	70	5.4	93	4.5	50	1.7	120	3.5
Co	25110	12	48250	1	31300	11	610	10	6700	6	ND	NA
Fe	2360	13	5020	0.5	3100	11	2700	5	880	7	1940	1
Mo	9650	13	11620	0.5	9830	11	2940	5	120	12.4	110	18.4
Ni	ND	NA	15	10.5	ND	NA	14	13.2	120	11	210	0.7
S	200	23	240	6	50	24	360	8	6880	6	6250	2.1
ND: Not detectable; NA: Not applicable

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Graphical abstract

A method for the complete digestion of carbon nanostructures has been demonstrated. Photographs (on the left side) show zirconium crucibles containing SWCNTs with flux of Na_2CO_3 and K_2CO_3 , before and after microwave fusion; (on the right side) the appearance of the final solutions containing dissolved samples, from microwave-assisted fusion and microwave-assisted acid digestion. These solutions were used for determining the trace elemental impurities by ICP– OES.