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Use of Raman Spectroscopy to Identify Carbon Nanotube Contamination at an Analytical Balance Workstation

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Abstract

Carbon nanotubes (CNTs) are cylindrical molecules of carbon with diverse commercial applications. CNTs are also lightweight, easily airborne, and have been shown to be released during various phases of production and use. Therefore, as global CNT production increases, so do concerns that CNTs could pose a safety threat to those who are exposed to them. This makes it imperative to fully understand CNT release scenarios to make accurate risk assessments and to implement effective control measures. However, the current suite of direct-reading and off-line instrumentation used to monitor the release of CNTs in workplaces lack high chemical specificity, which complicates risk assessments when the sampling and/or measurements are performed at a single site where multiple CNT types are handled in the presence of naturally-occurring background particles, or dust. Herein, we demonstrate the utility of Raman spectroscopy to unequivocally identify whether particulate matter collected from a multi-user analytical balance workstation comprised CNTs, as well as, whether the contamination included CNTs that were synthesized by a Ni/Y-catalyzed electric-arc method or a Co/Mo-catalyzed chemical vapor deposition method. Identifying the exact CNT type generated a more accurate risk assessment by knowing the metallic impurities involved, and it also led to the identification of the users who handled these CNTs, a review of their handling techniques, and an improved protocol for safely weighing CNTs.

Keywords

nanosafety; nanomaterial workplace exposure; nanomaterial occupational hygiene; safely handling nanopowders

INTRODUCTION

Carbon nanotubes (CNTs) are an allotrope of carbon that come in two basic varieties. The first is a single-walled CNT (SWCNT) that can be represented as a graphene sheet of sp^2 -hybridized carbon atoms seamlessly wrapped into a cylindrical tube. The diameter of an individual SWCNT is typically 0.7–1.5 nm and the electronic structure can be metallic, semi-metallic, or semi-conducting depending on how the graphene sheet is rolled up. The second are multi-walled CNTs (MWCNTs) that can have as many as fifty SWCNTs nested

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within one another and diameters greater than 100 nm. The lengths of SWCNTs and MWCNTs can range from a few nanometers to a few centimeters and their ends can be open or closed.⁽¹⁾ CNTs can be synthesized by a variety of methods resulting in materials comprising different CNT structures and dimensions, as well as, different types and amounts of metallic and carbonaceous impurities.⁽²⁾

CNTs possess unique electronic, optical, thermal, and mechanical properties that make them promising agents for use in the broad areas of composite materials, sensors, electronics, and energy storage.^(1,3–5) CNTs are also under development for a variety of biomedical applications including artificial muscles, tissue scaffolds, and the detection and treatment of diseases.^(6–9) It is this diversity of exciting applications and market opportunities that is driving a steady growth in the worldwide production of CNTs, currently estimated to exceed several thousand tons per year.^(1,10) However, as CNT production increases, so does the possibility for human exposure.⁽¹¹⁾ This is concerning since there is a growing body of evidence that even small amounts of some CNTs can pose a health risk if they are inhaled, ingested, or absorbed through the skin.^(12–21) The greatest concern is perhaps respiratory exposure since the toxicity associated with inhaling (sub)micron-sized particles is well established and since it is now recognized that lightweight CNTs can be released during various stages of their application life cycles.^(22–25) For example, CNTs have been shown to be released during synthesis, harvesting, reactor cleaning, transferring to containers, weighing, milling, sonicating, spraying, and machining of materials containing CNTs.^(26–34)

A variety of direct-reading and off-line instruments have been used alone and in combination to monitor the release of CNT particulate matter from dry powders, liquid suspensions, and solid composite materials.^(24,35–39) The most commonly used direct-reading instruments for CNT assessments include aerodynamic particle sizers (APSs),^(26–29,40) condensation particle counters (CPCs),^(26,27,29,30,33,34,41) optical particle counters (OPCs),^(26,30,41) scanning- and fast-mobility particle sizers (SMPSs/FMPSs),^(26–29,34,40–42) electrical low pressure impactors (ELPIs),^(41,42) diffusion chargers (DCs),^(33,41) and differential mobility analyzers (DMAs).^(26,34) These real-time methods can provide measures of the surface area, number concentration, mass concentration, and/or electrical mobility of particles either directly or through calculations using particle size distributions; they are, however, insensitive to particle composition and geometry.^(35,38) Information concerning particle composition and/or geometry is typically assessed using more sophisticated analytical instrumentation after particles are collected from a workplace, typically using filter papers. The most commonly used off-line instruments for assessing the release of CNTs include thermal-optical (TO) detectors that can measure elemental and organic carbons,^(31,33,41) laser induced breakdown spectrometers (LIBSs) that can identify metal-containing CNTs,⁽³²⁾ and most notably, a scanning or transmission electron microscope (SEM/TEM) with an energy-dispersive x-ray (EDX) analyzer that can detect all elements in a sample between atomic numbers 4 and 92.^(26–34,40–42) Nonetheless, all of these direct-reading and off-line instruments lack high chemical specificity for nanostructured carbons. This can complicate risk assessments especially when the sampling and/or measurements are performed at a site where multiple carbon nanomaterial (CNM) types are handled in the presence of naturally-occurring background particles, or dust – a complex mixture of plant pollen, mammalian hair and skin cells, textile and paper fibers,

minerals from the soil, vehicle emissions, and potentially many other inorganic and organic materials.^(29,34,36–38,43)

Our laboratory operates a multi-user analytical balance workstation where twenty different CNM powders are weighed and where it is impossible to visually decipher if particulate matter surrounding the balance is dust or CNM contamination. Microprobe Raman microscopy was chosen to analyze particulate matter collected from this workstation for the following reasons. First, there are a number of resonances common to sp²-carbon systems that can be used to unambiguously confirm the presence of nanostructured carbons in a contamination sample. Second, the spectral features of these resonances, in particular, the tangential stretching mode (G-band) at ~1582 cm⁻¹ and the second-order disorder mode (G'-band) at ~2600 cm⁻¹, can be used to distinguish one CNM (e.g., a SWCNT, MWCNT, fullerene, or graphene oxide) from another.^(44,45) And third, if radial breathing modes (RBMs) are observed between ~150–350 cm⁻¹, they can be used to unequivocally determine if a sample contained SWCNTs, as well as, whether a SWCNT-containing sample contained metallic and/or semi-conducting SWCNTs.⁽⁴⁶⁾ Using this approach, we first show that particulate matter collected on filter papers from three regions of the analytical balance workstation indeed contained SWCNTs. Furthermore, using a Raman spectral database of reference dust and the CNMs used at this workstation, we could determine whether the SWCNTs in these contaminated samples were one of the seven Ni/Y-catalyzed electric-arc synthesized SWCNT products or one of the five Co/Mo-catalyzed chemical vaporization deposition (CVD) synthesized SWCNT products used at this workstation. Thus, the use of Raman spectroscopy increased our ability to understand the risk and implement improved control measures. Specifically, knowing the exact type of SWCNT materials generated more accurate assessments of the potential toxicological hazards involved because the metallic impurity levels of these products were known, and additionally led to the identification of the users who handled these SWCNTs. This in turn led to a review of our CNM handling protocols and a better understanding of the difficulties in handling lightweight static materials, resulting in the development of improved protocols and training for safely weighing CNMs.

METHODS

Materials

All CNMs were purchased as dry powders and were used as-received. Caution, extreme safety precautions must be followed when handling CNM powders;⁽⁴⁷⁾ for example, a contoured, well-fitted, HEPA-filter air-purifying facepiece respirator and other personal protective equipment (PPE) such as Z87-rated eyewear, a long-sleeve lab coat, and nitrile gloves must be worn at all times as detailed in the Supplemental Information. As-produced SWCNT soot (product AP, lot AP-421), purified pristine SWCNT soot (product P2, lots 02-406 and 02-419), carboxylated SWCNT soot (product P3, lots 03-A018, 03-A010, and 03-180), and carboxylated and lyophilized SWCNT soot (product Ly-P3, lot 03-A009FD) were purchased from Carbon Solutions Inc. (Riverside, CA); all of these products were synthesized by a Ni/Y-catalyzed electric-arc discharge method. Pristine SWCNT soot (product SG-65, lot 0031; product SG-76, lot 0013; and product SWeNT, lots NI3-A005,

UT3-A003, and UT3-A002) were purchased from Southwest Nanotechnologies Inc. (Norman, OK); all of these products were synthesized by a Co/Mo-catalyzed CVD method. Short pristine MWCNT soot (product SP-M10; lot 1236YJS-041709), long pristine MWCNT soot (product LP-M10; lot 1205YJ-031010), short carboxylated MWCNT soot (product SC-M10; lot 1256YJF-070510), and long carboxylated MWCNT soot (product LC-M10; lot 1269YJF-102411) were purchased from Nanostructured & Amorphous Materials Inc. (Houston, TX); all of these products were synthesized by a Fe/Co/Ni-catalyzed CVD method. Single-layer graphene oxide powder (product SLGO) was purchased from Cheap Tubes Inc. (Cambridgeport, VT). As-produced fullerene soot (product 572497), spherical glassy carbon powder (product 484164), and graphite powder (product 282863) were purchased from Sigma Aldrich Inc. (St. Louis, MO). Thermogravimetric analyses of CNM powders to estimate the weight percentages of metals was performed as described previously.⁽⁴⁸⁾ Millipore 37-mm diameter quartz fiber filter (QFF) papers were purchased from Fisher Scientific Inc. (Houston, TX).

Microprobe Raman Spectroscopy

All Raman spectra acquisition methods were similar to those described previously.⁽⁴⁹⁾ Spectra were acquired utilizing a Horiba Jobin Yvon high-resolution LabRam Raman microscope system equipped with a 250- μm entrance slit and an 1100- μm pinhole. The 633-nm laser excitation was provided by a Spectra-Physics model 127 helium-neon laser operating at 20 mW. A 50 $\times$ /0.5 NA LM-Plan objective was used with a neutral density filter of 0.6 and the power density emanating from this objective was typically 3.4 mW as measured using a Newport model-1815C power meter with an 818-UV series photodetector. Wavenumber calibration was performed using the 520.7 cm^{-1} line of a silicon wafer and the spectral resolution was $\sim 1 \text{ cm}^{-1}$. The acquisition time for each spectral region was 1 s with a sub-pixel setting of 3 to enhance band definition by 3 fold. The minimum overlap of spectral windows was set to 50, and all spectra were plotted as the average of two accumulations.

Reference Raman spectra of the as-received CNMs utilized in this laboratory were acquired from samples prepared by placing a (sub)milligram amount of the CNM powder directly onto a clean QFF paper that was housed in the bottom of a Petri dish. This was accomplished by placing a Teflon-coated spatula into the CNM container followed by gently tapping the spatula onto the QFF paper to transfer the powder from the spatula to the QFF surface. Immediately after a CNM was transferred to the QFF, the lid was placed over the dish to contain the CNMs during transport to the spectrometer. Reference dust samples acquired from locations where CNMs were not handled or stored were processed in the same manner except that forceps were used to place dust particles onto the QFF surface. Particulate matter from the analytical balance workstation was collected by placing a QFF paper on the chosen surface region and applying slight pressure to transfer material from the surface to the QFF paper. In all cases, the Petri dish was placed on the microscope stage and particles were brought into focus by viewing white-light images obtained through a video camera with the path of the 633-nm laser blocked. Next, the 633-nm laser was focused directly on the center of a chosen particle and Raman spectra were acquired with the white light turned off.

RESULTS

This laboratory maintains an analytical balance workstation where as many as a dozen researchers use Teflon-coated spatulas to transfer ~1-mg amounts of a CNM powder (typically comprising (sub)micron-sized aggregates of individual CNMs) out of its original container and into a dram vial residing on the balance pan (Figure 1). The standard operating procedure (SOP) used by these researchers is presented in the Supplemental Information. The primary intentions behind this SOP are to describe methods to handle lightweight CNMs in order to minimize the contamination of non-vented workplace areas with CNMs and the exposure of personnel to CNMs, to properly clean CNM contamination, to properly dispose of CNM waste, and to provide recommendations for suitable personal protective equipment (PPE) that should be used during these operations.^(13,25,38,50,51)

The first step in using microprobe Raman spectroscopy to analyze particulate matter collected from this analytical balance workstation was the evaluation of the 633-nm Raman spectrum of the filter paper used to collect the particulate matter, in this case, QFF papers approved by the U.S. EPA for use with air-collection devices and personnel exposure badges. As shown in Figure 2, the Raman spectrum of a clean QFF paper is essentially featureless and there are no major intensities in the spectral regions where characteristic CNM peaks are expected to be observed.

The first workplace surface to be analyzed was the region underneath the analytical balance shown in Figure 3. This region was not typically inspected nor regularly cleaned due to recommendations that sensitive balances should not be moved or jarred. The material collected on the QFF paper from this surface is shown in Figure 4 as is a representative Raman spectrum from one of the particle-containing regions of this QFF. This spectrum clearly displayed a number of Raman peaks characteristic of SWCNTs, such as RBMs at ~143 cm⁻¹ and ~157 cm⁻¹, a disorder-induced mode (D-band) at ~1324 cm⁻¹, a G-band at ~1575 cm⁻¹, a second-order mode (SOM) at ~1756 cm⁻¹, the high-frequency iTOLA combination mode at ~1915 cm⁻¹, and a G'-band at ~2617 cm⁻¹. The spectra of particulate matter collected from this site were compared to the 633-nm Raman spectral database of reference dust and the twenty CNM products handled at this analytical balance workstation. In all cases, the material collected was unambiguously identified as containing Ni/Y-electric-arc synthesized SWCNTs, almost certainly the 03-180 lot of P3-SWCNTs (comprising <1 wt.% metals) based on the similarities in the spectral profiles and positions of the RBM peaks, the iTOLA mode, and the D-, G-, and G'-bands (Supplemental Figure 3 and Table 1).

The second workplace surface to be analyzed was the stainless-steel surface in the back-left corner of the analytical balance workstation shown in Figure 1. The material collected on the QFF paper from this surface is shown in Figure 5 as is a representative Raman spectrum from one of the particle-containing regions of this QFF. This spectrum clearly displayed a number of Raman peaks characteristic of SWCNTs, such as RBMs between ~210–280 cm⁻¹, a D-band at ~1296 cm⁻¹, a SOM peak at ~1716 cm⁻¹, an iTOLA mode at ~1898 cm⁻¹, a G'-band at ~2588 cm⁻¹ and a G-band comprising a G⁺-peak at ~1576 cm⁻¹ and a G⁻-peak at ~1538 cm⁻¹, a result of vibrations along the length (G⁺) and circumference (G⁻) of a pristine CNT. The spectra of particulate matter collected from this site were compared

to the 633-nm Raman spectral database and the contamination was unambiguously identified as containing pristine Co/Mo-CVD synthesized SWCNTs, almost certainly the 0013 lot of SG-76 SWCNTs (comprising ~7 wt.% metals) based on the similarities in the number and positions of RBM peaks, and the spectral profiles and positions of the SOM peak, iTOLA mode, and the D-, G⁺-, G⁻-, and G'-bands (Supplemental Figure 4 and Table 2).

The third workplace surface to be analyzed was a region outside of the enclosure ~36 cm above the air table (Figures 1 and 6A). This region was also not regularly cleaned as evidenced by the large amount of material collected on the QFF paper from this site (Figure 6B). Two distinct spectra were acquired from this QFF paper. The first distinct Raman spectrum from one of the particle-containing regions of this QFF is shown in Figure 7. This spectrum did not display any Raman peaks characteristic of CNMs but instead displayed a broad fluorescence-like background nearly identical to reference dust spectra B and C shown in Supplemental Figure 8. In fact, countless spectra resembling dust were observed from particulate matter collected on QFF papers used to sample surfaces of the analytical balance workstation and its surroundings throughout the course of this on-going investigation (data not shown). Nonetheless, while this demonstrates that microprobe Raman spectroscopy can be used to identify naturally-occurring background particles, it should be noted that the observation of dust-like spectra from a QFF does not rule out the presence of CNMs on a QFF paper unless a spectrum of every particle on the QFF is acquired. While such a task is impractical using most microprobe Raman instruments, this approach will benefit from recent advances in large-area laser scanning confocal Raman imaging systems that can automatically acquire high-resolution Raman spectra across the entire surface of a 37-mm diameter QFF paper.

The second distinct Raman spectrum acquired from this same QFF paper is shown in Figure 8. This spectrum clearly displayed a number of Raman peaks characteristic of SWCNTs, such as RBMs at ~141 cm⁻¹ and ~161 cm⁻¹, a D-band at ~1316 cm⁻¹, a G-band at ~1575 cm⁻¹, a SOM peak at ~1730 cm⁻¹, an iTOLA mode at ~1918 cm⁻¹, and a G'-band at ~2608 cm⁻¹. The spectra of particulate matter collected from this site were compared to the 633-nm Raman spectral database and the contamination was unambiguously identified as containing Ni/Y-electric-arc synthesized SWCNTs, almost certainly the 03-A009FD lot of Ly-P3-SWCNTs (comprising ~14 wt.% metals) based on the similarities in the spectral profiles and positions of the RBM peaks, SOM peak, iTOLA mode, and the D-, G-, and G'-bands (Supplemental Figure 3 and Table 1).

DISCUSSION

The combined results were alarming and prompted a re-evaluation of the weighing SOP and training protocols. The self-assessment started with an evaluation of the techniques and skill levels of all users, in particular those identified to be handling the SWCNT products identified on the QFF papers. In the case of the first two datasets where SWCNT contamination was observed on surfaces within the enclosed region of the analytical balance workstation (Figures 3–5), the major findings were that users were not thoroughly cleaning the workstation after use and that one user was inappropriately using compressed air to clean under the balance pan. The weighing SOP was aptly revised and disseminated to all users,

the surfaces within the enclosed region of the analytical balance workstation were thoroughly cleaned, and QFF samples from these surfaces were acquired more frequently (initially after each individual use of the balance) to confirm this situation was remedied across all users. In the case of the third dataset where SWCNT contamination was observed outside the enclosed region of the analytical balance workstation (Figures 6 and 8), this finding indicated that SWCNTs either became airborne during the weighing procedure and/or were transferred by a user(s) or circulating laboratory air. Regardless of the route, this finding prompted a complete cleaning of the analytical balance workstation surroundings and a second re-evaluation of our weighing SOP and training protocols. The major finding this time was that regardless of the technical skills and experience of a user, it is difficult to handle and weigh fine, dry CNM powders when the relative humidity is below 30%, particularly in the winter months when the relative humidity in the laboratory can be as low as 13%. Humidity control measures are being evaluated as are operator-protection hoods although these can sometimes interfere with the weighing process when the air draw is too high. A final notable PPE improvement advocated by a reviewer was the use of HEPA-filtered facepiece respirators.

CONCLUSIONS

An over-riding theme in many governmental reports and initiatives is the need for improved measurement techniques for monitoring engineered nanomaterials in realistic conditions during their life cycles in order to minimize uncertainties in identifying nanomaterial hazards. Herein, we demonstrated the utility of Raman spectroscopy to unequivocally identify whether particulate matter collected from a multi-user analytical balance workstation comprised SWCNTs, as well as, whether the contamination included SWCNTs that were synthesized by a Ni/Y-catalyzed electric-arc method or a Co/Mo-catalyzed CVD method. Knowing the exact SWCNT product generated a more accurate risk assessment by knowing the type and amount of metal impurities associated with the SWCNT contamination, and the inclusion of the toxicological profiles of these metals into the overall risk assessment, as first demonstrated and emphasized by Maynard et al.⁽²⁶⁾ Knowing the exact SWCNT product also led to the identification of the users who handled these SWCNTs, a review of their handling techniques, a better understanding of the difficulties in handling lightweight static materials, and an improved protocol for safely weighing CNMs. Looking forward, the feasibility of using Raman spectroscopy as an off-line technique for analyzing particulate matter collected on filter papers will be aided by recent advances in large-area Raman imaging systems that can additionally provide semi-quantitative particle-size information and that can be applied to the risk assessments of any Raman-active metal or metal oxide nanoparticle such as silver and titanium oxide nanoparticles.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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FIGURE 1.

Image of the analytical balance workstation analyzed in this work. The balance sits on an air table inside a five-sided, non-vented $3.8' \times 2.2' \times 2.0'$ enclosure.

FIGURE 2.

Image (inset) and representative 633-nm Raman spectrum of the smooth surface of a clean 37-mm diameter quartz fiber filter (QFF) paper.

FIGURE 3.
Image of the surface underneath the analytical balance shown in Figure 1.

FIGURE 4.

A representative 633-nm Raman spectrum of dark material collected on to a QFF paper (inset) that was used to sample the surface underneath the analytical balance shown in Figure 3.

FIGURE 5.

A representative 633-nm Raman spectrum of dark material on QFF paper (inset) collected from the back-left corner of the analytical balance workstation shown in Figure 1.

FIGURE 6.

Images of (A) a region outside the enclosed analytical balance workstation described in Figure 1 and (B) the QFF paper used to collect material from this region as denoted by the arrow.

FIGURE 7.

A representative 633-nm Raman spectrum of particulate matter collected on the QFF paper shown in Figure 6B.

FIGURE 8.

A second representative 633-nm Raman spectrum of particulate matter collected on the QFF paper shown in Figure 6B.