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The importance of an extensive elemental analysis of single-walled carbon nanotube soot

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Abstract

Few manufacturers provide elemental analysis information on the certificates of analysis of their single-walled carbon nanotube (SWCNT) soot products, and those who do primarily perform surface sensitive analyses that may not accurately represent the bulk properties of heterogeneous soot samples. Since the accurate elemental analysis of SWCNT soot is a requisite for exacting assessments of product quality and environmental health and safety (EH&S) risk, the purpose of this work was to develop a routine laboratory procedure for an extensive elemental analysis of SWCNT soot using bulk methods of analyses. Herein, a combination of carbon, hydrogen, nitrogen, sulfur, and oxygen (CHNS/O) combustion analyses, oxygen flask combustion/anion chromatography (OFC/AC), graphite furnace-atomic absorption spectroscopy (GF-AAS), and inductively coupled plasma-mass spectroscopy (ICP-MS) were used to generate a 77-element analysis of two as-received CoMoCAT[®] SWCNT soot products. Fourteen elements were detected in one product, nineteen in the other, and each data set was compared to its respective certificate of analysis. The addition of the OFC/AC results improved the accuracy of elements detected by GF-AAS and ICP-MS, and an assessment was performed on the results that concluded that the trace elemental impurities should not pose an EH&S concern if these soot products became airborne.

1. Introduction

All single-wall carbon nanotube (SWCNT) manufacturing processes use a carbon feedstock, metal catalysts, and heat to yield a heterogeneous powdered soot that contains a variety of SWCNT chiralities, non-tubular carbons such as amorphous carbon and graphitic nanoparticles, metals encased in these carbon phases, and in some cases, catalyst support material such as silica. The chemical and physical characterization of SWCNT soot is therefore very challenging, and measurement priorities and protocols for working with SWCNT soot have been documented in a number of practical guides that recommend the use of a host of analytical methods (including elemental analysis) for a thorough

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examination [1–10]. Five of the most common methods used by manufacturers to qualify soot quality are: high-resolution electron microscopy (EM) to estimate the amounts of SWCNTs and non-tubular carbons [1,2,5], NIR spectroscopy to generate a relative SWCNT purity factor [11,12], UV-Vis-NIR spectroscopy to determine the abundance of semi-conducting, semi-metallic, and metallic SWCNTs [13,14], Raman spectroscopy to generate a relative SWCNT quality factor [15,16], and thermogravimetric analysis (TGA) to estimate the percentages of metallic and carbonaceous components in SWCNT soot [17,18]. While the resultant quality metrics from these qualitative analyses are not directly comparable, the main advantage of the latter four bulk methods of analysis are that they generate statistically relevant data reflecting the underlying properties of the ensemble soot sample [5,7].

Few manufacturers provide elemental analysis information on their SWCNT soot certificates of analysis, but those who do primarily use x-ray photoelectron spectroscopy (XPS) or energy-dispersive x-ray spectroscopy (EDS). The advantage of these techniques lie in the number of elements they can detect; specifically, XPS can detect all elements except for hydrogen and helium [19], and EDS can detect all elements between atomic numbers 4 and 92 [20]. The disadvantage of using these surface sensitive techniques for the analysis of a heterogeneous powder stems from their high spatial resolution. Specifically, XPS has a depth resolution of $<100 \text{ \AA}$ and a lateral resolution of $10 \text{ }\mu\text{m} - 2 \text{ mm}$ [19, 21–23], and EDS systems associated with electron microscopes have a depth resolution of $0.3 - 5 \text{ }\mu\text{m}$ and a lateral resolution of $0.5 \text{ }\mu\text{m}$ [24–26]. It is therefore prohibitively expensive and time consuming to obtain enough discrete XPS or EM-EDS spectra to accurately represent the bulk properties of a SWCNT soot sample.

Surprisingly, bulk methods of analysis such as carbon, hydrogen, nitrogen, sulfur, and oxygen (CHNS/O) combustion analyses and inductively coupled plasma-mass spectroscopy (ICP-MS) are rarely used to provide elemental analysis information on SWCNT soot certificates of analysis. The strengths of CHNS/O and single-quadrapole ICP-MS are that they are rapid, readily accessible, and relatively inexpensive instruments when compared to other sensitive elemental analysis techniques such as neutron activation analysis (NAA) and prompt gamma activation analysis (PGAA) [27]. ICP-MS advantages include a nine decade analytical working range for much of the periodic table and detection limits that are at or below the part per trillion (ppt) level; disadvantages include high Si detection limits, the inability to analyze C, H, N, S, O, and elements without naturally occurring isotopes (i.e., most radioactive elements), and difficulties in determining elements that form negative ions such as halides [28,29]. While the union of CHNS/O and ICP-MS for the analysis of SWCNT soot seems obvious, we have only observed four works concerning their use to partially characterize CNT soot products. The first report by Korneva involved a three element CHN analysis of multi-walled CNT (MWCNT) soot [30], the second by Plata et al. involved the use of CHN analysis and ICP-MS to assay for 55 elements in eleven SWCNT soot products [31], the third by Zeisler et al. involved the use of NAA and ICP-MS to assay for 30 elements in SWCNT soot [27], and the fourth report by Cherkasov et al. involved the use of CHNS/O analysis and TGA-MS to assay for seven elements in MWCNT soot [32]. Surprisingly, many ubiquitous elements, such as halides and oxygen, were not analyzed in these works. For example, only one work reported a weight percentage for oxygen [32], and only one work reported a weight percentage for chloride [27]. Furthermore, while three of

these works analyzed for expected metals (i.e., metal catalysts specific to the particular CNT synthetic method) [27,31,32], only one work assayed for silicon catalyst support material [31], and only two attempted a partial survey of unexpected elements stemming from proprietary post-synthetic processes, contact with equipment in the manufacturing environment, and miscellaneous handling tasks such as sub-division into discrete containers [27,31].

Since a thorough characterization of SWCNT soot is imperative for exacting assessments of product quality and environmental health and safety (EH&S) risk [6,9,33–38], the primary goal of this work was to develop a routine laboratory procedure for an extensive elemental analysis of SWCNT soot using readily-available bulk methods of analysis. The ancillary goals were to keep costs to a minimum to facilitate monitoring of batch-to-batch variability, which is often overlooked by end users [6], and to minimize sample size requirements to <100 mg, in cases where the amount of sample was limited. To achieve this, a combination of CHNS/O analysis, graphite furnace-atomic absorption spectroscopy (GF-AAS), ICP-MS, and oxygen flask combustion/anion chromatography (OFC/AC) were chosen to generate a 77-element analysis of two as-received CoMoCAT® SWCNT soot products – essentially all elements on the periodic table that are not radioactive or noble gases (Supplemental Figure 1). Fourteen elements were detected in one product, nineteen in the other, and each data set was compared to its respective certificate of analysis. The addition of the OFC/AC results was shown to improve the accuracy of elements detected by GF-AAS and ICP-MS, and an assessment was performed on the results that concluded that the trace elemental impurities should not pose an EH&S concern if these soot products became airborne.

2. Experimental

2.1. Nanomaterials

Two products (I and II) of CoMoCAT® SWCNT soot (1.0 g each) were obtained from SouthWest NanoTechnologies Inc. (Norman, OK, USA). The 2009 product-I soot was enriched with (7,6) SWCNTs by the manufacturer (Lot No. SG76-0013) while the 2005 product-II soot was not (Lot No. UT4-A001). Caution, a fine-particulates respiratory mask and other personal protection equipment (PPE) should be worn when handling dry soot [39]. Both soot samples were analyzed as-received and were stored in their original containers. Sub-samples were withdrawn after containers were inverted three times.

2.2. CHNS/O Analyses

All CHNS/O analyses were performed by Micro-Analysis, Inc. (Wilmington, DE, USA) using a Perkin Elmer 2400 Series II CHNS/O Analyzer. The CHNS analyses were based on the Pregl-Dumas technique using a furnace temperature of 1100 °C. Samples were combusted completely in the presence of excess oxygen, and NO_x gases were reduced to N₂. Product gases (CO₂, H₂O, SO₂, and N₂) were captured in a mixing chamber and homogenized before being separated using gas chromatography with thermal conductivity detection. The results were reported as percent by weight of each element with a precision of ±0.30% and a limit of detection (LOD) of <0.10%. The analytical ranges for each element were: carbon 0.001 – 3.6 mg, hydrogen 0.001 – 1.0 mg, nitrogen 0.001 – 6.0 mg, and sulfur

0.001 – 2.0 mg. The oxygen analysis was based on the Unterzaucher technique using a pyrolysis furnace temperature of 1100 °C and an atmosphere of 95% He/5% H₂. Reaction products containing oxygen are converted to CO over platinized carbon, passed through a scrubber, separated, and quantified using gravimetric detection. The results were reported as percent by weight with a precision of $\pm 0.30\%$ and a LOD of $<0.10\%$. The analytical range for oxygen was 0.001 – 2.0 mg. The minimum sample size requirement for a CHNS analysis was 20 mg of soot and that for an oxygen analysis was 10 mg.

2.3. Raman Spectroscopy

Raman spectra were acquired using a Jobin Yvon Horiba HR800 high-resolution LabRam Raman microscope system 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. Spectral acquisition was performed with a 1.0-s integration time, a minimum overlap of 50, and a 3-subpixel average. Wavenumber calibration was performed using the 520.5 cm^{-1} line of a crystalline Si wafer. Soot samples were prepared by heating in air from room temperature to 1000 °C at a rate of 10 °C/min in an alumina pan, and spectra were acquired directly from the alumina pan. Spectra of as-received soot were acquired on a Si wafer after sub-samples were suspended in aqueous surfactant.

2.4. OFC/AC Analyses

All OFC/AC analyses were performed by Micro-Analysis, Inc. and were based on the Schöniger flask technique in which 10-mg samples were electrically ignited (or ashed) in an oxygen-filled flask to convert elements to their ionic forms. The resulting solution is diluted and filtered before analysis using anion chromatography with conductivity detection. The results were reported as percent by weight of each element with a precision of $\pm 0.30\%$ and a LOD of $<0.10\%$ for fluoride, chloride, and bromide, and a precision of $\pm 0.30\%$ and a LOD of $<0.25\%$ for iodide. The minimum sample size requirement for an OFC/AC analysis was 40 mg of soot (10 mg per non-radioactive halide).

2.5. GF-AAS

All GF-AAS analyses for silicon were performed by Precilab, Inc. (Carrollton, TX, USA) using our previously reported digestion protocol [18]. A calibration was established using a blank solution and standards of 50 ppb, 100 ppb, and 150 ppb Si prepared from a 1000 ppm Si standard (Inorganic Ventures, Christiansburg, VA, USA). Samples were analyzed using the 251.6-nm line of Si at a final furnace temperature of 3000 °C with a Varian AA280Z GF-AAS spectrometer employing Zeeman background correction. Results were reported in ppm and the method detection limit (MDL) for silicon was 1.50 ppb. The minimum sample size requirement for a GF-AAS analysis was 5.0 mg of soot.

2.6. ICP-MS Analysis

All ICP-MS analyses were performed by Precilab, Inc. using our previously reported acid digestion protocol [18]. In brief, a solution of 100 μL of 37% HCl and 100 μL of 69% HNO₃ was added to 5–10 mg of sample which was bath sonicated for 20 min and then allowed to

sit overnight. Next, the sample was diluted with a 2% HNO₃ blank to a total volume of 50 mL. All metals were calibrated using blanks and standards of 0.050 ppb, 0.100 ppb, 0.250 ppb, and 0.500 ppb concentrations of the respective metals prepared from 1000 ppm standard solutions (Inorganic Ventures); the internal standard was rhodium 103. The samples and standard solutions were aspirated through a nebulizer into a torch chamber and then injected into the ~10,000 K plasma through argon gas flow. The determination of Al, Ca, Cr, Fe, Li, Mg, Mn, Ni, K, and Na was performed using a Thermo X Series ICP mass spectrometer or a Thermo X-II Series ICP mass spectrometer in cool mode (a 600 W plasma). The determination of Ag, As, Au, B, Ba, Be, Bi, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Lu, Mo, Na, Nb, Nd, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr was performed using a Varian 820MS ICP mass spectrometer in hot mode (a 1400 W plasma). Elements were classified as <LOD if the observed amounts were at or below the respective MDL for that element (Supplemental Table 1). The minimum sample size requirement for a 67-element ICP-MS analysis was 5.0 mg of soot.

3. Results and Discussion

3.1. CHNS/O and OFC/AC Analyses

The CoMoCAT[®] SWCNT soot products used in this work were synthesized by a catalytic chemical vapor deposition (CVD) method involving a bimetallic cobalt-molybdenum catalyst. While the exact conditions will vary for different products, in general, the catalyst is supported on a silicon dioxide substrate and heated to 700 – 1000 °C at 1 – 10 atm before a carbon source such as carbon monoxide or methane is introduced. The reported purification process involves removing amorphous carbons by air oxidation at <300 °C, dissolving metal oxides with hydrochloric acid, dissolving silicon dioxide with hydrogen fluoride, and rinsing the remaining material with deionized water until the pH is neutral [41–43].

The following approach to generate an extensive elemental analysis of SWCNT soot involves summing the weight percentages of elements detected by the CHNS/O and OFC/AC analyses, and using GF-AAS and ICP-MS to determine the identity and amount of elements that are not C, H, N, S, O, or halides. However, the first step is to ensure that all carbon nanomaterials present in a soot product (i.e., SWCNTs and non-tubular carbons) will be combusted by the 1100 °C furnace temperature selected for the CHNS and O analyses. Raman spectroscopy was chosen to analyze combusted soot owing to a number of well-characterized vibrational bands unique to carbon nanomaterials such as the disorder-induced mode (D-band) at ~1300 cm⁻¹, the tangential stretching mode (G-band) at ~1590 cm⁻¹, the second-order G'-band at ~2600 cm⁻¹, and in the case of SWCNTs, radial breathing modes (RBMs) in the 150 – 350 cm⁻¹ region [40]. Supplemental Figures 2 and 3 show representative Raman spectra from soot products I and II before and after each was heated to 1000 °C. In both cases, characteristic carbon nanomaterial peaks (i.e., a D-band, G-band, G'-band, or RBMs) were not observed in either product after heating, which was expected since the SWCNTs and non-tubular carbons in CoMoCAT[®] soot have been shown to have oxidation temperatures <1000 °C [14,18]. Nonetheless, it is still prudent to confirm the

complete combustion of carbon nanomaterials in unique SWCNT soot products with respect to the particular heating parameters of a CHNS/O instrument.

The CHNS/O results for products I and II are listed in Table 1. Carbon was the most abundant element observed in both soot products implying that SWCNTs and non-tubular carbons were the major components. The level of carbon detected in product I was ~83% and was ~78% for product II. These levels are similar to the ~81% carbon levels reported by Plata et al. [31], but are lower than the ~96% carbon levels reported by Zeisler et al. [27], who both analyzed various CoMoCAT[®] SWCNT soot products. Trace (<1%) levels of hydrogen were detected in products I and II suggesting low levels of hydrogen-terminated amorphous carbon, adsorbed hydrogen gas, and polycyclic aromatic hydrocarbons (PAHs). This is important because trace levels of toxic PAHs, formed at elevated temperatures from the incomplete burning of carbon species, have been observed in a variety of electric arc discharge- and CVD-synthesized SWCNT products [31,44]. Trace (<0.4%) levels of nitrogen were detected in the soot products suggesting low levels of adsorbed nitrogen gas and toxic N-heterocyclic compounds that can be formed during synthesis of SWCNTs [31].

Oxygen was the second most abundant element observed in both soot products. The level of oxygen present in product I was ~9% and ~10% in product II (Table 1). Since CoMoCAT[®] SWCNT soot is not purified using oxidizers like HNO₃, these SWCNTs are not expected to contain a high degree of oxygen functional groups. It is therefore most likely that the oxygen observed is associated with salts and metal oxide impurities and not oxygen-containing functional groups on the surfaces of the SWCNTs and non-tubular carbons. This is supported by the observation that the pristine CoMoCAT[®] soot products were immiscible in water, which is in contrast to the moderate water solubility observed with oxidized SWCNTs.

OFC/AC was chosen to determine halide content since this method was more sensitive than the available ICP-MS method. The OFC/AC results for products I and II are listed in Table 2. Fluoride was the most abundant halide observed in both soot products; its level in product I was ~1% and the level in product II was <0.3%. The level of chlorine present in both products I and II was <0.2%. In combination with the low H results, the F and Cl data imply that adequate rinsing procedures were performed to remove any HCl and HF used in the purification process. In summary, the combined weight percent of the six elements detected (C, H, N, O, F, Cl) in product I was 94.67% and that for the five elements detected (C, H, N, O, F) in product II was 89.50%.

3.2. GF-AAS and ICP-MS Analyses

The results of the CHNS/O and OFC/AC analyses were reported as percent by weight of each element analyzed (Tables 1 and 2, respectively). To determine the identity and amount of elements in the remaining masses (5.33% in product I and 10.50% in product II), GF-AAS was selected to assay for Si and ICP-MS was selected to assay for 67 other elements; calculations used to report the resulting elemental percentages (Table 3) are described in Supplemental Figure 4.

GF-AAS was chosen to assay for traces of silicon dioxide. In brief, the GF-AAS MDL for Si was lower than the ICP-MS MDL, and a high resolution (HR)-ICP-MS was not available. The amount of Si detected in product I (~134 ppm) was 13-fold more than that detected in product I, but was significantly lower than the ~2,000 ppm SiO₂ reported by Plata et al. who also analyzed a CoMoCAT[®] SWCNT soot product [31]. The low levels of silicon detected in products I and II indicates that most of the residual silicon dioxide substrate was dissolved by HF and rinsed away.

The concentrations of elements determined by ICP-MS are shown in Supplemental Table 2 and the calculated percentages are shown in Table 3. As expected, molybdenum and cobalt were the most abundant metals observed in both CoMoCAT[®] soot products with levels as high as ~24,000 ppm Mo and ~4,000 ppm Co in product II. While the Mo and Co levels in product II were ~3× more than those observed in product I, this observation is not concerning since the ratio of each catalyst can be tailored to generate unique SWCNT products [43]. However, the presence of catalytic metals in purified soot products does suggest that metals were encased by a carbonaceous shell which hindered their dissolution by acids [45]. Six additional elements (Al, Ca, Fe, Na, Si, and Sn) were detected in product I while twelve additional elements (B, Ba, Ca, Ce, Fe, La, Mg, Na, Nd, Ni, Pb, and Y) were detected in product II (Table 3). The detection of some of these elements was expected since metals from the manufacturing environment can be transferred to soot during post-synthetic treatments with acids [31], as was the presence of other elements owing to the ubiquitous presence of salts in laboratory environments.

One important aspect of an extensive elemental analysis is an improvement to the accuracy of the overall determination. In the present approach, a complete CHNS/O analysis and the addition of the OFC/AC analysis improved the accurate weight percent determination of elements detected by GF-AAS and ICP-MS. In other words, if the significant weight percentages of oxygen (8.96%) and fluoride (1.02%) observed in product-I soot were omitted from the calculations described in Supplemental Figure 4, then all elements determined by GF-AAS and ICP-MS would be erroneously reported with higher weight percentages. This is noteworthy because when considering the previous use of CHNS/O analyzers to perform elemental analyses of CNT soot [30–32], two works did not perform oxygen and sulfur analyses [30,31], and none performed an assay for the four non-radioactive halides. In summary, the sum of the fourteen elements detected in product I was 99.98% and the sum of the nineteen elements detected in product II was 100.00% (Tables 1–3).

3.3. EH&S Assessment of Elemental Impurities

The EH&S implications of metals in aerosolized SWCNT soot were first reported by Maynard et al. who represented the exposure level for an element as the product of the airborne level of SWCNTs during handling and the concentration of the element in the SWCNTs [46]. In brief, using SWCNTs containing Fe and Ni, they determined that airborne-SWCNT levels of 53 µg/m³ corresponded to an airborne exposure level of up to 14.5 µg Fe/m³, which is four orders of magnitude lower than the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for Fe, and to an airborne

exposure level of up to $1.3 \mu\text{g Ni/m}^3$, which is three orders of magnitude lower than the OSHA PEL for Ni (Supplemental Table 3).

To assess if any of the elements present in soot products I and II could pose an EH&S concern if these SWCNTs became airborne, the method of Maynard et al. was applied to the major elements detected in the CoMoCAT[®] soot products shown in Table 3. In addition, it was applied to the additional eleven product-I elements and eighteen product-II elements shown in Supplemental Table 2 whose observed concentrations were above the respective MDL for that element, but accounted for less than 0.01% of the total mass of the respective soot sample. For example, using the 55 ng/mg concentration of Pb in product II and an airborne-SWCNT value of $53 \mu\text{g/m}^3$ (reported by Maynard et al. [46]), the calculated exposure level for Pb in soot product II would be 2.9 ng/m^3 . Since this value is four orders of magnitude lower than the $50 \mu\text{g/m}^3$ PEL for Pb (Supplemental Table 3), the Pb in product II should not pose a significant EH&S concern if this product became airborne. In fact, after performing this calculation for the remaining elements listed in Supplemental Table 3 (including the most abundant element, Mo, and the elements with the lowest PELs, Cr and Cd), it was determined that none of the elements with an available OSHA PEL should pose a significant EH&S concern if these soot products became airborne. It should be noted, however, that while these airborne impurity levels are lower than the PELs, there is considerable debate about the most relevant time interval over which exposure should be measured so as to include the associated risks of impurity accumulation [46].

While similar approaches could be applied to EH&S assessments of the elemental impurities of soot in aqueous environmental or biological samples using other metrics (e.g., a half maximal inhibitory concentration (IC₅₀) or lethal dose (LD₅₀)), the heterogeneity of SWCNT soot and the bioavailability of elemental impurities further complicates such investigations; for example, Liu et al. showed that nickel in a variety of SWCNT samples was bioavailable at toxicologically significant concentrations despite its apparent encapsulation by carbon [47]. In addition, there is now increasing evidence that impurities can play a critical role even when present in extremely low amounts; for example, the inhibitory concentration of cationic yttrium released from SWCNTs that potentially interfered with the calcium ion channel function of tsA201 kidney cells was 70 ppb [48]. In summary, assessments like these illustrate the importance of a full-scan (67-element) ICP-MS analysis of soot to identify and quantify expected and unexpected elements, especially since there are significant variations in SWCNT synthetic methods, post-synthetic treatments, and handling practices amongst manufacturers. In addition, it illustrates the importance of an extensive elemental analysis, not only for assessing product quality and batch-to-batch consistency, but for avoiding the possibility of falsely attributing potential toxicity to SWCNT soot when the source of toxicity could have been an elemental impurity contained within the soot.

3.4. Comparisons to Certificates of Analyses

The certificate of analysis for the product-I CoMoCAT[®] SWCNT soot reported a carbon content of 91.80% based on TGA. TGA is by far the most prevalent bulk analysis method used by manufacturers to assess batch-to-batch consistency because it can rapidly provide the number of distinct components in a CNT soot sample. However, TGA is semi-

quantitative at best with peak fitting errors as high as 20% for CNT soot samples [17], especially soot samples displaying broad TGA derivative peaks as this is an indication of a material with a plurality of chemical components. For example, several common salts and metal oxides display oxidation temperatures similar to those of SWCNTs, and thus, if these contributions are not accounted for, it is possible for the TGA-determined carbon weight percentage to be overestimated. As a result, the use of TGA to provide an estimate of carbon and metal weight percentages requires a number of assumptions and additional spectroscopic investigations performed on residual soot material remaining at various stages of the TGA run. This also makes it extremely difficult to use TGA to estimate the weight percentages of SWCNTs and non-tubular carbons; in fact, we have previously observed non-tubular carbon Raman spectral signatures in TGA peaks assigned to SWCNTs, and vice versa [49]. In conclusion, while it is erroneous to compare the 83.48% elemental carbon value determined using a CHNS/O analyzer (Table 1) to a carbon weight percentage determined by TGA, these factors likely explain the discrepancy between the two values.

Six elements (C, O, Mo, Co, F, and Si) totaling 100.26% were identified by XPS and reported on the certificate of analysis for the product II CoMoCAT[®] SWCNT soot (Tables 1–3). In comparing these elemental percentages to those obtained for product II using the combination of CHNS/O, OFC-AC, GF-AAS, and ICP-MS, the certificate's carbon level was overestimated by ~18%, the oxygen value was underestimated by ~3-fold, the molybdenum value was underestimated by ~10 fold, and cobalt, fluoride, and silicon were not detected. In fact, the surface-sensitive XPS analysis did not detect sixteen of the nineteen major elements reported by the combined bulk analysis methods. Part of the reason for these discrepancies is the <100 Å depth resolution and the <2 mm lateral resolution of XPS, as well as, the possibility that elements (most notably, metal catalysts) can be encased within a thick (<10 nm) carbonaceous shell and thus hidden from the X-ray beam [8,25,26,31,45]. Ultimately, it is not that the XPS analysis is inaccurate, but rather, that it is representative only of the area(s) probed by the survey- or high resolution-scan(s).

5. Conclusion

The starting material for all applications of SWCNTs is a heterogeneous multi-component soot, and the compositions of commercially-available soot products vary according to manufacturers' synthetic methods, post-synthetic treatments, and handling practices. Extensive elemental analyses are therefore needed for the accurate assessment of product quality and EH&S risk. Herein, four bulk methods of analysis (i.e., CHNS/O, OFC/AC, GF-AAS, and ICP-MS) were used to generate a 77-element analysis of SWCNT soot – essentially all elements on the periodic table that are not radioactive or noble gases. These instruments were chosen due to accessibility and the convenience of using previously developed methods; they could be interchanged with others techniques such as laser induced breakdown spectroscopy (LIBS), ICP-optical emission spectroscopy (OES), or HR-ICP-MS, which could be used for the sensitive detection of additional elements such as phosphorous. Two as-received CoMoCAT[®] SWCNT soot products were analyzed, fourteen elements were detected in one product, nineteen in the other, and discrepancies with their certificates of analysis were discussed. It is anticipated that the combined use of these readily-available bulk methods should find wide applicability to the analysis of a variety of carbon

nanomaterials because as little as 80 mg of sample is required to perform a complete analysis, in cases where the amount of sample is limited, and because pilot studies have demonstrated the feasibility to determine the elemental composition of graphene, graphene oxide, and pristine and carboxylated MWCNT powders.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:

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Table 1

CHNS/O results for CoMoCAT[®] SWCNT soot products I and II.

Element	Product I Mean $\pm$ CI (%)	Product II Mean $\pm$ CI (%)
C	83.48 $\pm$ 1.56	78.25 $\pm$ 9.08 [*]
H	0.70 $\pm$ 0.17	0.55 $\pm$ 0.06
N	0.38 $\pm$ 0.05	0.35 $\pm$ 0.25
S	<LOD	<LOD
O	8.96 $\pm$ 6.42	10.11 $\pm$ 5.34 [*]

Notes: The elemental percentages represent the means and 95% confidence intervals (CIs) from n = 3 independent measurements of product I and n = 2 of product II for the CHN determination, n = 2 of product I and n = 1 of product II for the sulfur determination, and n = 2 of products I and II for the oxygen determination. The LOD for the sulfur determination was 0.10%.

^{*} The product-II certificate of analysis reported 96% carbon and 3.4% oxygen by XPS.

Table 2

OFC/AC results for CoMoCAT[®] SWCNT soot products I and II.

Element	Product I Mean $\pm$ CI (%)	Product II (%)
F	1.02 $\pm$ 0.19	0.25 [*]
Cl	0.14 $\pm$ 0.89	<LOD
Br	<LOD	<LOD
I	<LOD	NA

Notes: The elemental percentages represent the means and 95% confidence intervals (CIs) from n = 2 independent measurements of product I. Due to limited sample, only n = 1 measurement of product II was performed and iodide was not analyzed (NA). The LODs for the determination of chloride and bromide were 0.10% and the LOD for the determination of iodide was 0.25%.

^{*} The product-II certificate of analysis reported 0.00% fluoride by XPS.

Table 3

Summary of major elements in CoMoCAT[®] SWCNT soot products I and II.

Element	Product I (%)	Product II (%)
Mo	4.51	8.73 *
Co	0.61	1.46 *
Ca	0.10	0.06
Si	0.04	n.d. *
Na	0.01	0.01
Fe	0.01	0.03
Sn	0.01	n.d.
Al	0.01	n.d.
B	n.d.	0.10
Pb	n.d.	0.02
Ce	n.d.	0.02
Ba	n.d.	0.01
La	n.d.	0.01
Mg	n.d.	0.01
Nd	n.d.	0.01
Ni	n.d.	0.01
Y	n.d.	0.01

Notes: Elemental percentages are listed in descending order of abundance with respect to product I. Elements were classified as not detected (n.d.) if they were observed below the GF-AAS or ICP-MS limit of detection (LOD), or if the observed amounts were above the respective LOD for that element but accounted for less than 0.01% of the total mass of the respective soot sample.

* The product-II certificate of analysis reported 0.86% molybdenum, 0.00% cobalt, and 0.00% silicon by XPS.