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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 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

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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 Å and a lateral resolution of 10 μm–2 mm [19,21–23], and EDS systems associated with electron microscopes have a depth resolution of 0.3–5 μm and a lateral resolution of 0.5 μm [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 Fig. 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 N_2. Product gases (CO_2, H_2O, SO_2, and N_2) 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,