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An investigation of carbon nanotube exposure assessment methods

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AN INVESTIGATION OF CARBON NANOTUBE EXPOSURE ASSESSMENT METHODS

by

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CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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ABSTRACT

Objectives: 1 To correlate carbon nanotube (CNT) concentrations measured by Method 5040 relative to particle count and volumetric concentrations; 2 to correlate CNT concentrations measured by Method 5040 relative to black carbon concentrations measured with an aethalometer; 3 to compare elemental carbon (EC) concentrations measured by Method 5040 among various CNT types and purities.

Methods: CNT samples were collected using 25 mm quartz fiber filters and analyzed for EC by Method 5040. An aethalometer was simultaneously used to measure black carbon concentrations. Samples sent for EC analysis included various CNT types (multi-walled, single-walled) and purities (high, low). Levels of EC concentration were subjected to a two-way analysis of variance having two levels of CNT type and two levels of purity.

Results: No correlation was established between CNT count and EC concentration, but a correlation was found between CNT volumetric and total carbon (TC) concentration. A significant correlation between black carbon and TC concentration was found. Method 5040 was found to have a positive bias for TC, and the aethalometer was found to have a positive bias for black carbon. Lastly, this study found that CNT type had no effect on EC concentration, but purity did have a significant effect on EC concentration.

Conclusions: Samples analyzed by Method 5040 were found to have 6 – 19% EC content, and thus surprisingly high amounts of organic carbon. The linear equation from the relationship found between TC concentration and black carbon concentration intercepted near zero indicating that the positive bias effects found with Method 5040 and the aethalometer appear to be removed. Future research is needed to investigate the aethalometer as a surrogate for Method 5040. Until then, those conducting CNT exposure

assessments should use a 25 mm cassette and increase the volume sampled to achieve a reporting limit lower than the NIOSH recommended CNT REL of 7 µg/m^3.

TABLE OF CONTENTS

LIST OF TABLES

Table

LIST OF FIGURES

Figure

CHAPTER I: LITERATURE REVIEW

Nanoparticles

Engineered nanoparticles are defined as particles with all dimensions smaller than 100 nm (ASTM E2456, 2006). Nanoparticles differ by physical dimensions (length, diameter, surface area) and physical properties (diffusivity, electrical, chemical, biological). Variation among nanoparticle properties gives rise to many potential applications, hence they are the subject of numerous multidisciplinary studies. A review of the four main processes by which nanoparticles are produced (gas-phase, vapor deposition, colloidal, and attrition) determined that each may potentially result in exposure by inhalation, dermal or ingestion routes (Aitken, et al., 2004). Exposure to nanoparticles in the work place raises concerns for safe handling practices as studies have shown that ultrafine particles contribute to adverse health effects in the respiratory tract as well as in extrapulmonary organs (Oberdörster, et al., 2005).

Carbon Nanotubes

Among nanoparticles, carbon nanotubes (CNT) are most commonly produced or used (Schubauer-Berigan, et al., 2011; Mishra, et al., 2012). In general, CNTs can be visualized as a single sheet of carbon atoms rolled into a scroll (single-walled carbon nanotube, SWCNT) with a diameter of a few nanometers. Multiple layers of carbon existing within each other, or tubes within a tube, bring about multi-walled carbon nanotubes (MWCNT). Structural differences among CNTs yield outstanding physical properties in terms of mechanical strength, electrical conductivity, and thermal or optical properties which offer many opportunities for industrial applications (Journet, et al., 2012).

Manufactured CNTs are intentionally engineered for commercial purposes with specific properties. Four main synthesis methods have been identified for CNTs: laser ablation, arc discharge, chemical vapor deposition, and plasma-enhanced chemical vapor

deposition (Hofmann, et al., 2003). Often CNTs are grown and produced at a primary manufacturing site before they are sent to secondary manufacturers where they may be incorporated into spray coating, semiconductor devices, mixing formulations, resins, and specialized plastics (Dahm, et al., 2012). Current applications of CNTs include flat panel display screens (Chen, et al., 2007), atomic force microscopy probe tips (Wilson & Macpherson, 2009) and CNT enhanced composites (Thostenson, et al., 2001). The global market for various CNT grades was estimated to generate nearly $239 million in revenues in 2012 and is projected to grow over the next five years, reaching $527 million by 2016 (BCC Research, 2012). With such potential growth in CNT applications and expanding use in occupational settings, the adverse health effects of CNT should be considered.

CNT Toxicity

Particle size plays an important role in determining the potential adverse effects of nanoparticles in the respiratory system by influencing the physical, chemical and biological nature of the material, by affecting the surface area dose of deposited particles, and by enabling deposited particles to more readily translocate to other parts of the body (NIOSH, 2009). The main routes of exposure to CNTs include the skin and lungs. Given that airborne CNTs are subject to the physics of impaction, sedimentation and diffusion, and because inhaled CNTs reach the distal regions of the lung, inhalation studies have been determined to more accurately model deposition and pathologic responses to occupational exposure scenarios compared to studies using CNT exposure to skin (Zhao & Liu, 2012).

Concern over CNT exposure within occupational settings arises from animal studies documenting CNT toxicity. Human bronchial epithelia cells dispersed with MWCNTs were found to affect genes involved in regulation of the brain, lungs, epithelium, liver and colon, as well as induce genes associated with neuropathy and

cancer (Kim, et al., 2011). *In vivo* inhalation studies on mice have shown that SWCNTs induced inflammatory response and fibrosis (Shvedova, et al., 2008), while MWCNTs suppress systemic immune function (Mitchell, et al., 2007) and induce pulmonary inflammation and fibrosis (Porter, et al., 2010). A complete review of several inhalation studies reported acute pulmonary toxicity, subpleural fibrosis, and immune suppression from CNT exposure to mice (Zhao & Liu, 2012). Overall, CNT exposure has the potential to cause early onset of pulmonary inflammation, oxidative stress, granuloma formations and fibrosis in rodents (Shvedova, et al., 2005; Shvedova, et al., 2008; Porter, et al., 2010).

Several studies have compared CNT-induced pulmonary effects to those caused by known hazards such as carbon black, crystalline silica and asbestos. The long yet thin structures of CNTs are similar to asbestos, both having high aspect ratios (>100) (Pint, et al., 2008). CNTs have been reported to induce granulomas and pulmonary inflammation to a higher extent than carbon black particles and fine crystalline silica (Shvedova, et al., 2005) while causing pulmonary inflammation and fibrosis at exposures equal to or greater than those caused by asbestos exposure (Muller, et al., 2005). Studies document that MWCNTs are able to reach visceral pleural tissue in the lungs after aspiration exposure and have penetrated alveolar macrophages and the alveolar wall (Porter, et al., 2010; Mercer, et al., 2010; Xu, et al., 2012). Materials with very large aspect ratios (e.g. asbestos) are not cleared effectively from the pleural cavity, which can result in deposition in the parietal pleura (Xu, et al., 2012), and initiate mesothelial injury and inflammation which over time leads to pleural mesothelioma (Donaldson, et al., 2010).

Assessing Aerosol Concentrations

Aerosol measurements are needed in order to assess CNT exposures in occupational settings. Count, mass and surface area are the three metrics used to quantify exposure to aerosols. Concentrations of nanoparticles can be expressed in terms of their

number, mass, or surface area per unit volume of air. Evaluating concentration by count is an attractive option since sensitive instruments are available.

On account of their optical properties, nanoparticles can be evaluated with light scattering instruments which are tuned to provide count- and mass-based concentrations. One such instrument is a condensation particle counter (CPC). Particles that enter the CPC grow to micrometer-sized droplets in a supersaturated environment and the change in light transmission before and after growth is related to the particle number concentration (Hinds, 1999). Alternatively, a scanning mobility particle sizer (SMPS) can be used to provide count and mass concentrations. The SMPS uses a technique based on size-fractionated aerosol sampling in which polydispered aerosol enters a differential mobility analyzer (DMA) and exits as nearly all singly charged and nearly monodisperse (Hinds, 1999). By varying the voltage across the DMA, the SMPS is able to count and size a distribution of particles. Evaluating concentrations by surface area is also available yet still under development. Historically, the most common metric used to evaluate nanoparticles among regulations is mass-based (NIOSH, 2009). As a consequence, evaluating CNTs can be very difficult as many display negligible mass when weighing samples gravimetrically.

The aethalometer is an instrument that measures the mass concentration of optically absorbing aerosol black carbon (a form of elemental carbon) particles in real time (Hansen, et al., 1984). The instrument operates on the principle of continuously measuring the attenuation of 880 nm light through a glass fiber filter as it loads over time. The attenuation through the filter is expressed as: attenuation = $-100 \ln (I/I_0)$, where I_0 and I are the intensities of the transmitted light through the loaded and blank filters, respectively (Gelencsér, 2004). Only a small spot on the filter is exposed to aerosol and the rest of the filter is blank. The aethalometer measures two channels: black carbon from the loaded filter spot and the blank reference area. Since the flow rate is held constant, the rate of deposition of black carbon onto the filter is proportional to its concentration in the

aerosol and gives a corresponding rate of increase in optical attenuation (Gelencsér, 2004).

Aethalometers can be used to investigate area or personal exposure to carbonaceous particles found in ambient air in occupational and environmental settings. Black carbon and elemental carbon (EC) measurements taken in various remote and urban environments have been found to have a consistently high correlation. A review of recent studies, published in the year 2000 or later, that compare ambient black carbon and EC measurements had an average correlation coefficient of 0.86 ± 0.11 (EPA, 2012).

Of the studies aimed at assessing CNT exposure in the workplace, few include black carbon concentration. Concentrations of black carbon have been reported between 7.8 and 321 $\mu g/m^3$ during the handling of MWCNTs in a laboratory and manufacturing plant (Han, et al., 2004; Lee, et al., 2010). Currently there are no occupational CNT exposure assessment studies which compare EC concentrations to black carbon concentrations.

Standards and Regulations

Several occupational exposure limits (OEL) have been proposed resulting from toxicological data indicating potential hazards from CNT exposure. In 2009 the Japanese New Energy and Industrial Technology Development Organization recommended an interim OEL for MWCNTs at 20 $\mu g/m^3$ (Kobayashi, et al., 2009). Later an OEL of 50 $\mu g/m^3$ was recommended based on the no-observed adverse effect level of a 13-week subchronic inhalation study on rats (Pauluhn, 2010). In November of 2010 the National Institute for Occupational Safety and Health (NIOSH) issued a draft Current Intelligence Bulletin on Occupational Exposure to Carbon Nanotubes and Nanofibers. Within the document NIOSH proposed a respirable, mass-based recommended exposure limit (REL) for CNTs of 7 $\mu g/m^3$ as elemental carbon (EC), a marker for CNT exposure (NIOSH, 2010). Although the Occupational Safety and Health Administration (OSHA) does not

have a permisible exposure limit (PEL) for carbon nanotubes, they acknowledge the NIOSH REL of 7 μg/m^3 and state that existing OELs may not provide adequate protection from exposure to CNT (OSHA, 2013).

Once black carbon exposure is determined it is compared to occupational exposure limits. For carbon black, the NIOSH REL is 3.5 mg/m^3 over a 10-hour time-weighted average while the OSHA PEL is 3.5 mg/m^3 over a 8-hour time-weighted average (NIOSH, 2013). Although black carbon is not the same as carbon black, both are materials consisting of high amounts of EC. Carbon black is produced by partial combusion or by thermal decomposition of hydrocarbons, whereas black carbon is a generic term for carbanacious byproducts resulting from incomplete combustion and may contain dichloromethane and toluene impurities (ICBA, 2006). The American Conference of Governmental Industrial Hygienists (ACGIH) has a category for unregulated compounds and has set an 8-hour time-weighted average limit of 3 mg/m^3 for respirable particles not otherwise specified (PNOS).

Sampling and Analysis

NIOSH Method 5040 (as elemental carbon) is the NIOSH proposed analytical method for measuring airborne CNTs (NIOSH, 2010). Samples are collected on 37-mm (or 25-mm) quartz-fiber filters in a 3-piece cassette using a flow rate within the range of 2 to 4 L/min. Thermal-optical analysis involves baking a filter portion (punch) of known area (typically 1.5 cm^2) in an oven at temperatures above 850°C while tranmitance is measured (NMAMa, 1994). Carbon present on the filter undergoes catalytic oxidation followed by a reduction to methane, which in turn is quantified using flame ionization detection (NMAMa, 1994). Quantities of organic carbon (OC) and EC are reported in micrograms per filter area. The method has a limit of detection (LOD) of 0.3 μg/filter portion area and does not report a limit of quantitation (LOQ). The LOQ is the lowest concentration at which elemental carbon can be detected reliably by Method 5040. The

reporting limit, or LOQ reported by an analytical lab, is the product of the LOD and the deposition area, reported in units of micrograms. The LOQ is converted to units of micrograms per air volume by dividing the LOQ (in units of micrograms per sample) by the air volume sampled. Thus, the final LOQ reported by an analytical lab depends directly on the filter size and indirectly on the air volume used during sampling. NIOSH reports an upper (high) LOQ of 7 $\mu g/m^3$ for Method 5040 (NIOSH, 2010).

CNT Exposure Assessments

In the past decade several studies have been directed at evaluating CNT exposures, the majority of which were conducted in laboratory settings. One such study assessed the release of aerosol particles from handling SWCNTs, finding that in the lab fine particles were released into the air with sufficient agitation (Maynard, et al., 2004). The study was conducted in four different manufacturing facilities where SWCNT material was handled and airborne CNT concentrations were found to be between 0.70 and 53 $\mu g/m^3$. Four of the five personal air samples taken at various field sites were above the NIOSH REL of 7 $\mu g/m^3$. All Exposure to CNT particles in a research lab during chemical vapor deposition (CVD) growth and during subsequent handling was investigated where no increase in the total particle number concentrations was detected using a real-time particle sizer and condensation particle counter (CPC) (Bello, et al., 2008). Total MWCNT particle concentrations in another laboratory-based study ranged from 37 to 430 $\mu g/m^3$ prior to implementing engineering controls, whereas black carbon concentrations peaked at 200 $\mu g/m^3$ using a portable aethalometer (Han, et al., 2008). Another study that evaluated CNT release during CVD synthesis found SWCNT and MWCNT particles released at concentrations as high as 10^7 particles/cm^3 for SWCNT and $4x10^6$ particles/cm^3 for MWCNT measured by a fast-mobility particle sizer (FMPS) and aerodynamic particle sizer (APS) (Tsai, et al., 2009). An alternative study generated CNT particles by dry cutting CNT composite materials with a band saw in a laboratory

and found airborne exposures at concentrations of 800 to 2400 µg/m^3 in the personal breathing zone measured by a FMPS and APS (Bello, et al., 2009).

Although laboratory-based assessments of CNT exposure are useful, they fail to capture real-world conditions occurring in occupational settings. Some studies have evaluated CNT exposures within industrial and manufacturing environments. One such exposure assessment study was conducted at seven different MWCNT manufacturing and handling work sites (industrial, research and laboratory sites) where personal sampling, area sampling and real-time monitoring took place (Lee, et al., 2010). Personal and area samples collected ranged from 7.8 to 160 µg/m^3 and 13 to 190 µg/m^3 where real-time monitoring involved a scanning mobility particle sizer (SMPS) and dust monitor. Additionally a portable aethalometer was used to measure total suspended particulates where maximum black carbon concentrations ranged from 500 to 4x10^6 µg/m^3. Another study performed air monitoring at six facilities (primary and secondary CNT manufacturers) using a CPC, photometer, and diffusion charger to monitor particle number, mass, and active surface area concentrations (Dahm, et al., 2012). Among both the primary and secondary manufacturing facilities, personal breathing zone samples collected ranged from 0.68 to 7.86 µg/m^3 EC while area sample concentrations ranged from 0.47 to 4.62 µg/m^3 EC. Of the total 52 samples taken for EC analysis 19 were found to be non detects by Method 5040 where the reported LOQ ranged between 0.71 – 1.7 µg EC per filter. Two personal breathing zone samples collected were above the NIOSH REL of 7 µg/m^3.

Specific Aims

NIOSH has determined that there is potential risk for developing adverse respiratory health effects if workers are exposed for a working lifetime at the upper LOQ of NIOSH Method 5040 (NIOSH, 2010). As it happens, the LOQ of Method 5040 is equal to the NIOSH REL for CNTs of 7 µg/m^3. The NIOSH REL presents an under- or

over-exposure scenario with no information to determine actual CNT exposure when measurements are below the Method 5040 LOQ. Therefore if CNT concentrations are below 7 $\mu g/m^3$, there may be little or no information on the actual magnitude of exposure provided by Method 5040.

The goal of this thesis is to establish a relationship between various exposure metrics that may be more sensitive than Method 5040 relative to concentrations measured using Method 5040. Metrics that will be compared with Method 5040 include count concentrations using a SMPS and mass concentrations using an aethalometer. The correlation between Method 5040 and aethalometer output will enable the use of an aethalometer in the field for personal exposure assessments for quantifying exposures at concentrations below the LOQ of NIOSH Method 5040. Study objectives will be accomplished through the following aims:

1. Correlate CNT concentrations measured with the use of Method 5040 relative to particle count and volumetric concentrations obtained in a system containing a CNT aerosol.
2. Correlate CNT concentrations measured with the use of Method 5040 relative to measurements made with a hand-held aethalometer.
3. Compare EC concentrations measured with the use of Method 5040 of pure CNTs with differing types and purities.

Table 1. CNT exposure assessment results and methods.

Reference	Process	CNT	Setting	Sample	Methods	Max Concentration
Maynard, et al., 2004	Handling	SWCNT	Production facilities	Personal	Method 7300	<53 μg/m^3
Han, et al., 2008	Handling	MWCNT	Research facility	Area	Method 7402	37 - 430 μg/m^3
				Area	Aethalometer	200 μg/m^3 BC
				Personal	TEM	193.6 tube/cm^3
Bello, et al., 2008	Handling (removal from substrate, harvesting)	Not specified	Laboratory	Area	FMPS; CPC	No change compared to background
				Area	TEM	ND
Bello, et al., 2009	Handling (dry cutting)	Not specified	Laboratory	Source PM_{10}	Dust track	2.11 and 8.38 mg/m^3
				Source	TEM	1.6 fibers/cm^3
Tsai, et al., 2009	Production	SWCNT	Field	Source	FMPS, APS	10^7 particles/cm^3
Lee, et al., 2010	Handling (CVD manufacturing, catalyst prep, ultrasonic dispersion, spraying, heating)	MWCNT	Plant	Personal	Method 7402	7.8 – 285.9 μg/m^3
				Fume hood	SMPS: DMA, CPC	7606 (0.014-0.25 μm) & 563 (0.25-32 μm) particles/cm^3
				Personal	Aethalometer	7.8 to 320.8 μg/m^3 BC
Birch, et al., 2011	Thermal treatment, reactor areas	CNF	Manufacturing facility	Respirable	Method 5040	3.41 - 80 μg/m^3 EC
Dahm, et al., 2012	Powder, aqueous forms in lab, handling (disposal, weighing, sonication)	MWCNT	Primary manufacturing facility	Personal	Method 5040	ND - 7.86 μg/m^3 EC
	Handling (transfer, weighing, mixing, sonication)			Personal	TEM	ND - 1.613 structure/cm^3

CHAPTER II: AN INVESTIGATION OF CARBON NANOTUBE EXPOSURE ASSESSMENT METHODS

Introduction

Carbon nanotubes (CNT) have grown in use and popularity over the past decade, becoming one of the most commonly produced and used engineered nanomaterials (Schubauer-Berigan, et al., 2011; Mishra, et al., 2012). The revenue of manufactured CNTs has been estimated to generate nearly $239 million in revenues in 2012 and are projected to reach $527 million by 2016 (BCC Research, 2012). Current applications of CNTs include flat panel display screens (Chen, et al., 2007), atomic force microscopy probe tips (Wilson & Macpherson, 2009) and CNT-enhanced composites (Thostenson, et al., 2001).

The adverse health effects of CNTs have been given much consideration in occupational settings. There is no epidemiological evidence of adverse health effects in workers resulting from CNT exposure, however animal studies have been used to determine CNT toxicity. The main routes of exposure to CNTs include the skin and lungs. The long yet thin structures of CNTs are similar to asbestos, both having high aspect ratios. CNTs have been reported to induce granulomas and pulmonary inflammation to a higher extent than carbon black particles and fine crystalline silica (Shvedova, et al., 2005) while causing pulmonary inflammation and fibrosis at exposures equal to or greater than those caused by asbestos exposure (Muller, et al., 2005). Both CNT type and purity may significantly influence CNT toxicity. Single-walled CNTs (SWCNT) and multi-walled CNTs (MWCNT) produce varying toxicological responses as a result of exposure (Donaldson, et al., 2006; Tian, et al., 2006; Fraczek, et al., 2008), while differences in purity also appear to affect CNT toxicity (Muller, et al., 2005; Tian, et al., 2006). Overall, animal studies report early onset of pulmonary inflammation,

oxidative stress, granuloma formations, and fibrosis (Shvedova, et al., 2005; Shvedova, et al., 2008; Porter, et al., 2010).

At this time, the analytical method recommended for quantifying CNT exposure is Method 5040 from the National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NIOSH, 2010). Historically, Method 5040 has been used to monitor diesel particulate matter as elemental carbon (EC). Given that CNTs are one of several EC allotropes, Method 5040 can be used to quantify CNT exposure. As reported by NIOSH in the 2010 draft Current Intelligence Bulletin on Occupational Exposure to Carbon Nanotubes and Nanofibers, the upper limit of quantitation (LOQ) of Method 5040 is 7 $\mu g/m^3$ (NIOSH, 2010).

Various parties have made an effort to control CNT exposure by establishing occupational exposure limits (OEL). In 2009 the Japanese New Energy and Industrial Technology Development Organization recommended an interim OEL for MWCNTs at 21 $\mu g/m^3$ based on the 37 $\mu g/m^3$ no-observed-adverse-effect level determined from a 4-week subchronic rat inhalation study (Kobayashi, et al., 2009). The following year a less conservative OEL of 50 $\mu g/m^3$ was recommended for MWCNTs based on the 100 $\mu g/m^3$ no-observed-adverse-effect level determined from a 13-week subchronic rat inhalation study (Pauluhn, 2010). In November of 2010 NIOSH proposed a respirable, mass-based recommended exposure limit (REL) for CNTs at 7 $\mu g/m^3$ (NIOSH, 2010), equal to the upper LOQ of NIOSH Method 5040. Assessing exposures with this method allows the determination of either an under- or over-exposure, yet provides little or no information to determine actual exposure conditions when below the LOQ. Given that exposure to CNTs should fall below the NIOSH REL, it is implied that the majority of measurements taken will then be below the NIOSH Method 5040 LOQ and possibly even the LOD. The Occupational Safety and Health Administration (OSHA) has acknowledged the NIOSH REL of 7 $\mu g/m^3$ stating that existing OELs may not provide adequate protection from exposure to CNTs (OSHA, 2013). The LOQ for Method 5040 is unique in that it spans a

range of concentrations. The actual reporting limit (the LOQ reported by an analytical laboratory) for Method 5040 depends directly on the air volume collected and inversely with the filter deposit area (NIOSH, 2010). Hence by using a smaller diameter filter than the one proposed in the method, and by increasing the volume of air sampled through the filter, either by increasing the flow rate or by sampling over a longer period of time, one can reduce the LOQ.

A review of published CNT exposure assessment studies over the past decade is summarized in Table 1. A number of those studies have found CNT exposure mass concentrations within the range of <53 to 430 $\mu g/m^3$ among airborne personal and area samples (Maynard, et al., 2004; Han, et al., 2008; Lee, et al., 2010). However few studies have been employed which use Method 5040 when determining CNT exposure. In 2012 a study conducted in primary and secondary CNT manufacturing facilities investigated occupational CNT exposure using Method 5040: EC concentrations ranged from 0.68 to 7.86 $\mu g/m^3$ among personal samples and 0.47 to 4.62 $\mu g/m^3$ within area samples (Dahm, et al., 2012). Two of the personal samples from this study exceeded the 7 $\mu g/m^3$ REL for CNTs; however, the majority of exposures were below Method 5040's LOQ and hence no exposure data was available. Another study used Method 5040 to analyze EC in carbon nanofibers, different from CNTs, in workers during fiber productions where respirable EC concentrations were between 3.4 and 32 $\mu g/m^3$ in personal samples and between 3 and 22 $\mu g/m^3$ in area samples (Birch, et al., 2011). Future effort is needed to provide information on the effectiveness of Method 5040 in determining CNT exposure since limited studies exist.

Aethalometers, which optically measure the concentration of black carbon at 880 nm, have been used in previous studies as an alternative CNT exposure assessment method. Black carbon is a generic term for carbanaceous byproducts of incomplete combustion, which have high EC content and possibly contain dichloromethane and toluene impurities (ICBA, 2006). CNT exposures investigated in various studies

identified black carbon concentrations up to 200 µg/m^3 during MWCNT handling at a research facility (Han, et al., 2008) and between 450 and 4,000,000 µg/m^3 during CNT handling (spraying, ultrasonic dispersion, wafer heating) at multiple CNT-manufacturing workplaces (Lee, et al., 2010). At this time, the aethalometer has not been used concurrently with NIOSH Method 5040 to determine whether it is an appropriate surrogate to assess CNT exposures. When CNT exposures are below the Method 5040 LOQ the aethalometer would be a useful surrogate when determining actual conditions below the NIOSH proposed REL.

Therefore, the purpose of this paper was to evaluate NIOSH Method 5040 and other CNT exposure assessment methods with the following aims: (1) correlate CNT concentrations measured with the use of Method 5040 relative to particle count and volumetric concentrations; and (2) correlate CNT concentrations measured with the use of Method 5040 relative to measurements made with an aethalometer; and (3) compare EC concentrations measured with the use of Method 5040 among various CNT types and purities.

Methods and Materials

CNT Aerosol

MWCNTs were obtained from Nanostructured & Amorphous Materials Inc. (Los Alamos, NM). A 0.5 mg/mL 95% MWCNT suspension was prepared using purified water (Q-Gard 1, Millipore, Billerica, MA) and was sonicated for 5 min. Subsequent suspensions were prepared by serial dilution. For each experiment, the suspension was sonicated for 5 min. Additional CNTs, 90% MWCNT and 90% SWCNT, were purchased from Nanostructured & Amorphous Materials Inc. (Los Alamos, NM) while 99% SWCNT was purchased from Cheap Tubes Inc. (Brattleboro, VT). Each of these suspensions were prepared at 0.08 mg/mL and diluted to 0.04 mg/mL.

A schematic diagram of the experimental apparatus is shown in Figure 1. CNT suspensions were aerosolized by drawing compressed air through a high-efficiency particle air (HEPA) filter into a Collison nebulizer (MRE 3 jet, BGI Inc., Waltham, MA) operating at 20 lb/in^2 and stirred (SP18425 Nuova, Thermolyne, Dubuque, IA). Aerosol passed through a heated, 2.54 cm diameter brass tube (CN45515, ThermoScientific) into a water vapor condenser consisting of a 1 L glass jar surrounded by ice water. To facilitate particle growth, the aerosol was neutralized (model 3077A, TSI, St. Paul, MN) before entering a sampling chamber by vacuum pump (DAA-V715-E13 GAST, IDEX Corp.) operating at 9 L/min.

EC and OC Analysis

CNT samples were collected using closed-face 3-piece 25-mm cassettes using quartz fiber filters (225-1824, Lot# 11013-7DBPASK-052, SKC Inc., Eighty Four, PA) and cellulose support pads (225-28, Lot# 12158-7DCPASK-030, SKC Inc., Eighty Four, PA). Air was pulled through these cassettes at 9 L/min using a vacuum pump. Filters were pre-weighed on a calibrated six-place balance (Model MT5, Mettler-Toledo Inc., Columbus, OH). CNTs were sampled over a 60-min sample period and then the filter was post-weighed to determine the mass deposited on the filter and the concentration of the CNT aerosol in the chamber by gravimetric analysis. Each day of sampling the mass of a blank filter was measured; the average blank filter mass (40.798 ± 0.005 mg) was used to calculate the balance LOD at 0.016 mg.

Over the entire course of the study 95 filter samples were collected; 24 of these were chosen to be analyzed for EC and OC by NIOSH Method 5040 at the Wisconsin Occupational Health Laboratory (Madison, WI). Samples that underwent EC and OC analysis were chosen based upon the aerosol mass concentration on the filter with the assumption that the majority of the mass concentration could be attributed to EC. Target aerosol mass concentrations included: 1, 3, 7, 15, 30, 60, 120 $\mu g/m^3$ as EC. Samples

included 95% MWCNT (n = 11), 90% MWCNT (n = 4), 99% SWCNT (n = 4), 90% SWCNT (n = 4), and a water-only sample (n = 1). The highest number of samples was conducted with 95% MWCNTs with the intention of that data being used for correlations. Since CNT type was thought to contribute to overall EC concentration, but that effect might differ across different purities, the 0.08 and 0.04 mg CNT/mL water suspension concentrations were used for each CNT type and purity so as to perform an analysis of variance.. Table 2 includes the suspension concentration that was inserted into the nebulizer, the aerosol mass concentration measured gravimetrically, and the Method 5040 results for EC and OC for all samples that were sent for analysis. No lab blank was analyzed for EC and OC analysis. One of the 95% MWCNT samples, with an aerosol mass concentration of 47 µg/m3, was sampled for 360 min and all four of the 99% SWCNT samples) were sampled for 180 min because there was no detectable mass on the filter after 60 min.

NIOSH Method 5040 includes collecting samples on 37-mm quartz filters which are analyzed by a thermal-optical analysis. Carbon present on the filter undergoes catalytic oxidation followed by a reduction to methane which in turn is quantified using flame ionization detection (NMAMa, 1994). Quantities of organic carbon (OC) and EC are reported in micrograms per total filter area.

Real-Time Aerosol Monitoring

The particle size distribution, ranging from 7 to 290 nm, was determined using a SMPS which consisted of an electrostatic classifier (model 3080, TSI, Shoreview, MN) equipped with a long-differential mobility analyzer (model 3081, TSI, Shoreview, MN) and condensation particle counter (model 3785, TSI, St. Paul, MN) operating at a flow rate of 1.0 L/min and at a time resolution of 5 min. CNT count concentration was measured for each sample using the SMPS, and later converted to volumetric concentration. A hand-held aethalometer (model AE51, AethLabs, San Francisco, CA)

was used to measure the mass concentration of black carbon particles in the the test chamber based on absorption of transmitted light. The aethalometer measured total suspended particulate matter (black carbon, expressed in ng/m^3) at a flow rate of 0.5 L/min at a time resolution of 5 min. The aethalometer flow rate and black carbon concentration on a blank filter was calibrated using microAeth flow software prior to each use.

TEM Analysis

95% MWCNTs were analyzed for characterization (general size, shape, and degree of agglomeration) and visual verification using a JEOL JEM-1230 TEM (JEOL USA Inc., Peabody, MA). Samples (n=2) travelled through the experimental apparatus and was collected on a TEM grid inside an electrostatic precipitator (ESPnano, Spokane, WA).

Statistical Analysis

Correlations and regressions were analyzed using Minitab (Minitab version 16.1, State College, PA) with a statistical significance at $\alpha = 0.05$. Levels of EC concentration were subjected to a two-way analysis of variance having two levels of CNT type (MWCNT, SWCNT) and two levels of purity (high, low). EC concentration was normalized by dividing the EC mass per sample by particulate matter mass measured gravimetrically. Similarly, a two-way analysis of variance was repeated using TC concentration as a response to the effects of differing CNT type and purity. Statistical correlations and regressions were analyzed using Minitab (Minitab version 16.1, State College, PA). Statistical significance was evaluated at $\alpha = 0.05$.

Results

EC and OC Analysis

The suspension, aerosol mass, EC, and OC concentrations are presented in Table 2 stratified by CNT type and purity. Any samples that were below the reporting limit (LOQ reported by the analytical laboratory) for Method 5040 are noted in Table 2.The reporting limit from the analytical lab was 2.3 µg/sample and sampled air volumes were either 540, 1620, or 3240 L. A water-only sample was analyzed and resulted in an EC mass concentration below the LOD and an OC mass concentration of 69 µg/m^3. Figure 2 shows the mean and standard deviation of carbon content by CNT type and purity. The 95% MWCNT samples had mean EC and OC concentrations of 19 ± 25 and 115 ± 46 µg/m^3, respectively while the 90% MWCNT samples had mean EC and OC concentrations of 12 ± 5 and 137 ± 28 µg/m^3, respectively. The 99% SWCNT samples had mean EC and OC concentrations of 15 ± 5 and 62 ± 14 µg/m^3 for EC and OC concentrations, respectively; while the 90% SWCNT samples had mean EC and OC concentrations of 6 ± 1 and 100 ± 6 µg/m^3, respectively. The mean EC content across all samples ranged from 6 to 19%, whereas the OC content across all samples ranged from 81 to 94%. Note that total carbon (TC) is the summation of the EC and OC fractions.

Real-Time Aerosol Monitoring

Total suspended particulate concentrations ranged from 15 to 89 µg/m^3 and 58 to 77 µg/m^3 for 95% and 90% MWCNT, respectively. The 99% and 90% SWCNT samples had total suspended particulate concentrations in the range of 32 to 39 and 40 to 47, respectively. HEPA-filtered air flowing through the sampling apparatus produced a black carbon concentration of 0.028 µg/m^3 and a non-detectable (negative) aerosol mass concentration.

Correlation and Regression Analysis

The aerosol mass concentration, measured gravimetrically, was plotted against EC and TC mass concentration in Figure 3. The statistical correlation between the aerosol mass concentration and EC concentration was not a significant relationship ($p = 0.18$). Six of the samples analyzed by Method 5040 were below the EC reporting limit of 2.3 µg/sample (not included in the correlation), hence subsequent data analysis utilized TC instead of EC. As shown in Figure 3, the linear relationship demonstrates that TC concentration increased with increasing aerosol mass concentration as indicated by an R^2 value of 0.83 and a significant slope ($p < 0.001$). However, the intercept of TC concentration appears to have a positive bias when there is zero mass concentration on the filter (intercept = 84 $\mu g/m^3$).

Another positive bias surfaced when aerosol mass concentration was plotted against black carbon concentration in Figure 4. The linear relationship indicates that black carbon concentrations increased with increasing concentration on the filter as suggested by an R^2 value of 0.89 and a significant slope ($p < 0.001$).

There was no correlation found between count concentration, as measured by the SMPS, and TC concentration ($p = 0.13$). When count concentration was converted to volumetric concentration by converting to unit-density spheres, a stronger, positive correlation resulted ($r = 0.81$; $p = 0.003$). As shown in Figure 5, the linear relationship between 95% MWCNT volumetric and TC concentrations had an R^2 value of 0.65, with a statistically significant slope ($p = 0.003$).

Black carbon and TC were plotted over all CNT types and purities in Figure 6; the Pearson correlation coefficient (0.97) confirms that black carbon and TC concentrations are strongly and positively correlated ($p < 0.001$). A strong linear relationship ($R^2 = 0.94$) between black carbon and TC concentrations demonstrates that the highest black carbon concentrations coincide with the highest TC levels. The water-only sample was not included in the regression analysis however, since it was determined that both TC and

black carbon displayed a positive bias when there was no detectable mass concentration on the filter.

When examining samples nearest the range of Method 5040's LOQ range, a significant correlation ($p = 0.035$) was established between black carbon and EC concentration but only when the regression analysis included samples between the reporting limit and 11 $\mu g/m^3$ ($n = 4$), with an outlier removed (Figure 7). The value calculated for R^2 was 0.93, indicating that 93% of the variability of the data is explained by the linear regression.

TEM Analysis

Figure 8 depicts 95% MWCNTs that travelled through the experimental apparatus, providing visual verification of CNTs. An individual 95% MWCNT can be seen in the top, center portion of the figure, as well as two agglomerated CNT structures. The 95% CNTs were several hundred nanometers in length and less than 100 nm in width. The average mobility diameter was measured from 7 to 290-nm, and the normalized particle size distribution with standard deviation for 95% MWCNTs is presented in Figure 9.

Statistical Analysis

A general trend of higher CNT purity corresponding to higher EC concentration can be seen in Figure 2, specifically for SWCNTs. Method 5040 results were analyzed for significantly different EC concentrations between MWCNT and SWCNT and between high and low purity using a two-factor ANOVA. At the 0.05 significance level the interaction and effect of CNT type were found to be insignificant: $F(1, 15) = 3.01$, $p = 0.11$) and $F(1, 15) = 1.02$, $p = 0.33$), respectively. However, the effect of CNT purity was found to be significant, $F(1, 15) = 9.81$, $p = 0.009$. Hence CNT purity has an effect on EC concentration, but not CNT type. The two-way analysis of variance which analyzed for significantly different TC concentrations between CNT type and purity found no

significant effects at the 0.05 significance level: type, $F(1, 15) = 0.37$, $p = 0.56$ and purity, $F(1, 15) = 3.49$, $p = 0.086$. The interaction effect was also insignificant, $F(1, 15) = 2.87$, $p = 0.12$). This finding indicates that CNT type and purity have no effect on TC concentration.

Discussion

From this study we expected to find a trend showing higher EC (and thus TC) concentration as CNT count concentration increased. An insignificant correlation between CNT count concentration and TC concentration was found; the Pearson correlation coefficient was 0.49 with a p-value of 0.13. This result indicates that TC concentration remains constant as count concentration measured by the SMPS increases. Dahm et al. found a significant relationship between EC concentration and CNT structure counts by TEM when an outlier was removed, suggesting that using an SMPS to determine count concentration is possible (2012). We would also expect to find a correlation between EC and count concentration measured by the SMPS, however correlations were examined using TC instead of EC. Since highly sensitive equipment (i.e. SMPS) is unable to distinguish between TC concentration as count increases, using a hand-held CPC in the field would not be useful for determining TC concentration.

By converting count concentration to volumetric concentration in the SMPS a significant correlation was found (Figure 5). The Pearson correlation coefficient was 0.81 with a p-value of 0.003. The linear regression equation was significant with a coefficient of determination of 0.65, indicating that 65% of the variability of the data can be explained by the linear regression. There may be other sources of variability that were not considered in this study that effect the relationship between TC and volumetric concentration. Also, there may be a non-linear relationship that better predicts the overall variability of the data, however we only tested for a simple linear regression. The regression equation, although significant, is not useful to an investigator because the

NIOSH REL for CNTs is by the EC content and not TC content. Among CNT samples there is no clear relationship between EC and TC. Furthermore, highly sensitive instrumentation (i.e. SMPS) would be required to use the relationship but the SMPS is a highly expensive instrument and impractical for personal monitoring.

The relationship between TC concentration in all CNT types and purities measured by Method 5040 and black carbon concentration measured by an aethalometer was investigated (Figure 6). A significant relationship was found between black carbon and TC concentrations as indicated by an R^2 value of 0.94 ($p < 0.001$). The water-only sample, which had an OC concentration of 69 $\mu g/m^3$ and no detectable EC concentration, was not included in the correlations because it was an outlier. The regression equation is able to predict more variability in the data, compared to the relationship between TC and volumetric concentration. Again, the relationship was found to be significant but will not prove useful to an investigator since the NIOSH REL for CNTs is by EC content.

A positive bias was seen within Figures 3 and 4 when TC concentration, and black carbon concentration were plotted against aerosol mass concentration measured gravimetrically, respectively. With TC concentration plotted against black carbon concentration, the bias appears removed as the intercept (-5.8) nearly crosses through the origin. Because of this, it is reasoned that the source of the bias was from the balance used for gravimetric analysis. The LOD for the balance was 16 µg.

Samples nearest the Method 5040 LOQ range were examined and a significant correlation between black carbon and EC concentration was found as well (Figure 7). The correlation was weak as it only contained four 90% SWCNT samples. The coefficient of determination (0.93, $p = 0.035$) confirms that EC concentration increases with increasing black carbon concentration. Since 93% of the variability of the data was explained by the linear regression there is much potential for using an aethalometer to quantify CNT exposures, especially when below the upper LOQ of Method 5040.

Lastly, this study examined the effects of CNT type and purity on EC and TC concentration. No significant effect was found between CNT type and EC concentration; however CNT purity was significant. CNT samples of higher purity (e.g. 99% SWCNT) can therefore be expected to contain higher EC content than the same type of CNT with lower purity (e.g. 90% SWCNT) as seen in Figure 2. However, CNT samples that differ by type (e.g. MWCNT and SWCNT) should not be expected to contain significantly different concentrations of EC. This information is highly useful for risk assessments knowing that different types of CNTs are equally hazardous but the most pure varieties will contain higher EC concentrations. For TC concentration, the effect of CNT type and purity were not found to be significant. Hence concentrations of TC will not change between samples of different CNT type, or by sample of differing purity.

Visual verification of 95% MWCNTs was presented in Figure 8. The 95% CNTs were several hundred nanometers in length and less than 100 nm in width. The general shape of the 95% MWCNTs varies from a single strand to CNT agglomerates. The normalized particle size distribution indicates that the most common particle size that was measured was approximately 20 nm with a number concentration of 660,000 #/cm^3. The 95% MWCNTs in Figure 8 had widths less than 100 nm, which was measured within the particle size distribution.

At this time it is unclear how the study samples obtained such high amounts of OC, yet there are several possible sources that have been considered. First, the quartz fiber filters and cellulose support pads used in this study have not been analyzed (blank) by Method 5040. For Method 5040 analysis quartz fiber filters are required to be heat-treated; the quartz filters purchased for the study were heat-treated by SKC prior to receiving them. It may have been beneficial to re-treat the filters prior to use. The cellulose support pads, which are primarily made of OC, could have left OC on the back of the filter. Another source of OC may be caused by impurities from compressed air that were able to penetrate through the HEPA filter, or from the deionized water used in the

study. The experimental apparatus could also be a source of OC. The water-only sample was conducted between 95% MWCNT samples. It would have been beneficial to sample for water prior to sending CNTs through the apparatus in order to have a better understanding of actual background conditions. An air-only sample was taken (again between 95% MWCNT samples) which had no detectable aerosol mass concentration measured by the SMPS, but had a detectable black carbon concentration of 0.028 $\mu g/m^3$ measured by the aethalometer. The air-only sample was not analyzed by Method 5040. Lastly, Method 5040 could be misreporting the actual amounts of EC and OC. Future analysis of laboratory blanks and method blanks is essential and will provide insight into the origins of the additional OC.

The LOQ for Method 5040 exists over a range. Since the LOQ is determined by multiplying the Method LOD by the deposition area, the LOQ is reduced by using a smaller filter. Hence a 25-mm filter is preferred over a 37-mm filter. Likewise, passing a larger volume of air through the filter will also lower the reported LOQ. Therefore I recommend that investigators use a 25-mm diameter filter and conduct sampling with large air volumes. Method 5040 offers a range of air volume within 142 to 19,000 L and suggest a flow rate within 2 to 4 L/min. As mentioned, this study used 9 L/min with air volumes of 540, 1620, and 3240 L. Resulting EC LOQs were 0.70, 1.4 and 4.2 $\mu g/m^3$, the lowest of which was achieved due to sampling over a 6-hour period. Sampling over such an extended period of time is possible as occupational exposure assessments often are conducted over a typical 8-hour period. However investigators interested in task-specific CNT exposures are likely to sample over a shorter periods. Exposure assessments which have been conducted on MWCNTs and CNFs using Method 5040 include Dahm et al. (2012) and Birch et al. (2011), respectively. Dahm et al. used a flow rate of 4.2 L/min while Birch et al., used a flow rate of 7 L/min. Both flow rates exceeded the suggested flowrate range of Method 5040. Birch et al. did not provide sampling times or air volumes, but Dahm et al. sampled with air volumes between 22 and 3400 L. Twelve of

the samples (14%) were under the minimum suggested air volume suggested by Method 5040. Overall, an investigator should be able to achieve a reporting limit below the NIOSH REL by using smaller filters (25-mm) and higher air volumes.

While developing and evaluating an analytical method, the method must have the ability to recover the analyte from the sampling medium. According to NIOSH, the method must be evaluated to determine whether on average, over a concentration range of 0.1 to 2.0 times the OEL, the method can provide a result that is within ±25% of the true concentration 95% of the time (NMAMb, 1994). In order to satisfy this requirement, the sampling concentrations must range from 0.7 to 14 $\mu g/m^3$. Given the reporting limit (LOQ provided from the analytical lab) of 4.3 $\mu g/m^3$, the lower end of the concentration range would not be reliably detected. Roughly 68% of the range can be reliably detected with this LOQ. If the upper LOQ of Method 5040 (7 $\mu g/m^3$) were obtained, less than 50% of the sampling range would be reliably detected. If estimated recovery does not exceed 75%, the method is not suitable for monitoring at this limit (NMAMb, 1994). At the upper LOQ, and at a reporting limit of 4.3 $\mu g/m^3$, the method appears to not meet NIOSH method requirements.

Limitations

The aims of this study were developed with the intent of correlating the EC fraction of CNTs with other exposure assessment methods. Hence a major limitation developed when the CNTs used in this study had little EC content (6 – 19%). Also, six of the samples analyzed by Method 5040 were below the reporting limit. In the future, CNT bulk samples should be analyzed for EC content by Method 5040 prior to aerosolized CNT samples.

In this study CNT aerosol was generated by introducing a known suspension concentration into the aerosolization system and each concentration was repeated at least twice. The final aerosol which reached the filter and aetholometer was highly variable

between samples and there were no replicated values of filter concentration, EC concentration or black carbon concentration. Hence it was impossible to include standard error within the data analysis. It is likely that if the CNT generation technique is improved, correlations will improve as well.

Gravimetric analysis performed throughout the study was conducted on a balance, and filters were stored in a chamber with desiccant. The quartz filters were a challenge to weigh at times, potentially because of any accumulated charge that effected the electrostatic balance. Even though filters were stored in desiccant overnight and neutralized before gravimetric analysis, many filters reported negative mass on them after sampling. There is potential for loss of the quartz fiber filter as some of the filters were damaged during the removal process from the cassette. A blank filter was weighed every day that sampling occurred and with this information the limit of detection of the balance was determined to be 16 µg. Gravimetric analysis would undoubtedly improve if a more sensitive balance were available in the future, or if the balance room was humidity controlled. The relative humidity in the balance room varied from < 20 to 54 %. In an ideal weighing environment the humidity would vary by ±5% for a relative humidity between 30 and 50% (Hinds, 1999).

Conclusions

Samples analyzed by Method 5040 were found to have 6 – 19% EC content, and thus surprisingly high amounts of OC. It is reasoned that significant amounts of impurities were introduced to CNT samples while travelling through the experimental apparatus. No correlation was established between CNT count concentration and EC concentration, but a correlation was found between CNT volumetric concentration and TC concentration. Through statistical analysis it was found that Method 5040 produced a positive bias for TC concentration when plotted against aerosol mass concentration. Likewise, black carbon measured by an aethalometer showed a positive bias when plotted

against aerosol mass concentration. When TC concentrations were plotted against black carbon concentrations a significant relationship was found and the bias appeared to cancel out. A significant relationship was also found between black carbon concentration and EC concentration near the upper LOQ of Method 5040, but only through four data points. Future research is needed to further investigate whether an aethalometer could be used as a surrogate method for Method 5040. Until then, those conducting CNT exposure assessments should use a 25-mm cassette and increase the volume sampled to ensure a reporting limit lower than the NIOSH recommended CNT REL of 7 $\mu g/m^3$. Lastly, this study found that CNT type had no effect on EC concentration, however purity was found to significantly effect EC concentration.

Table 2. Suspension, aerosol mass, EC, and OC concentrations relative to CNT type and purity.

Type	Purity, %	Concentration			
		Suspension, mg CNT/mL H_2O	Aerosol Mass, $\mu g/m^3$	EC, $\mu g/m^3$	OC, $\mu g/m^3$
MWCNT	95	0.08	146	81	120
		0.08	128	28	204
		0.04	72	30	165
		0.04	67	41	137
		0.02	41	< 2.1 [a]	128
		0.01	11	< 2.1 [a]	87
		0.01	57	< 2.1 [a]	106
		0.05	4	< 2.1 [a]	100
		0.05	22	< 2.1 [a]	94
		0.05	31	< 2.1 [a]	100
		0.003	47	17	25
MWCNT	90	0.08	39	4.4	106
		0.08	57	15	172
		0.04	106	15	130
		0.04	119	11	141
SWCNT	99	0.08	54	10	74
		0.08	51	20	74
		0.04	59	17	53
		0.04	49	12	48
SWCNT	90	0.08	56	5.4	91
		0.08	50	8.0	106
		0.04	19	6.7	102
		0.04	26	4.6	102
Water	100	0	0	< 2.1 [a]	69

[a]Results were below the reporting limit of 2.3 µg/sample

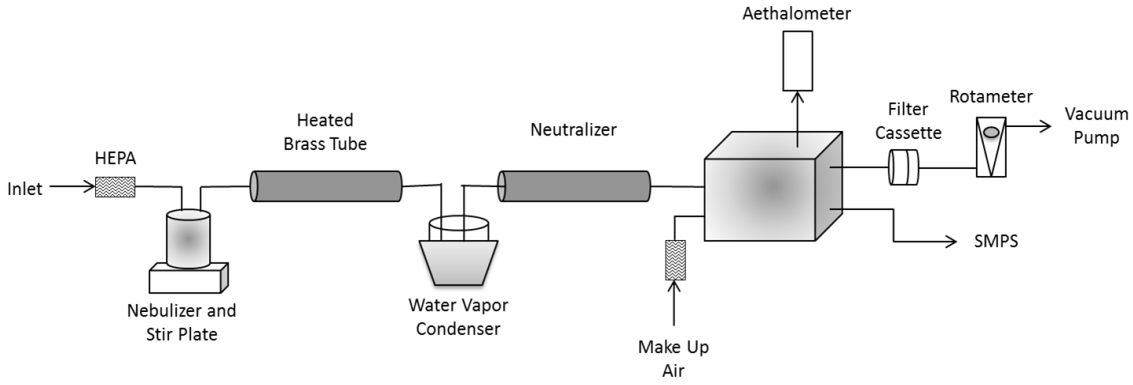

Figure 1. Diagram of the CNT aerosolization and sampling system.

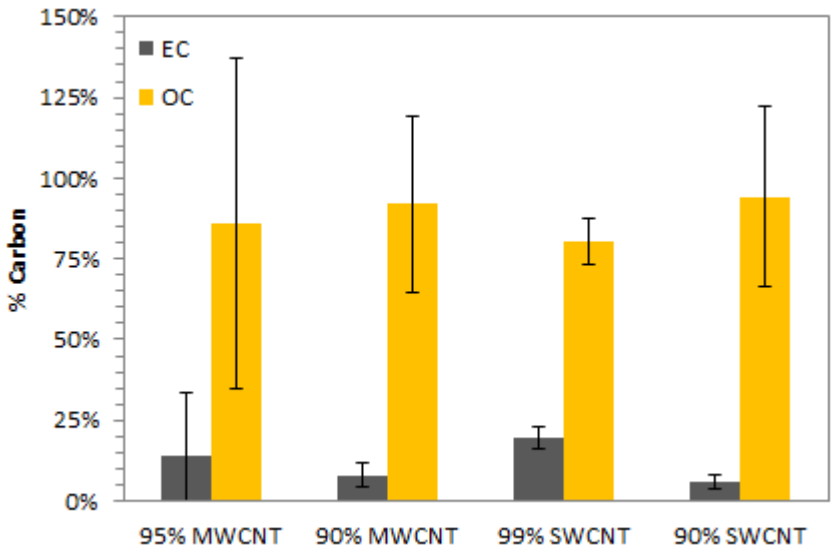

Figure 2. CNT type and purity by carbon content (mean ± standard deviation).

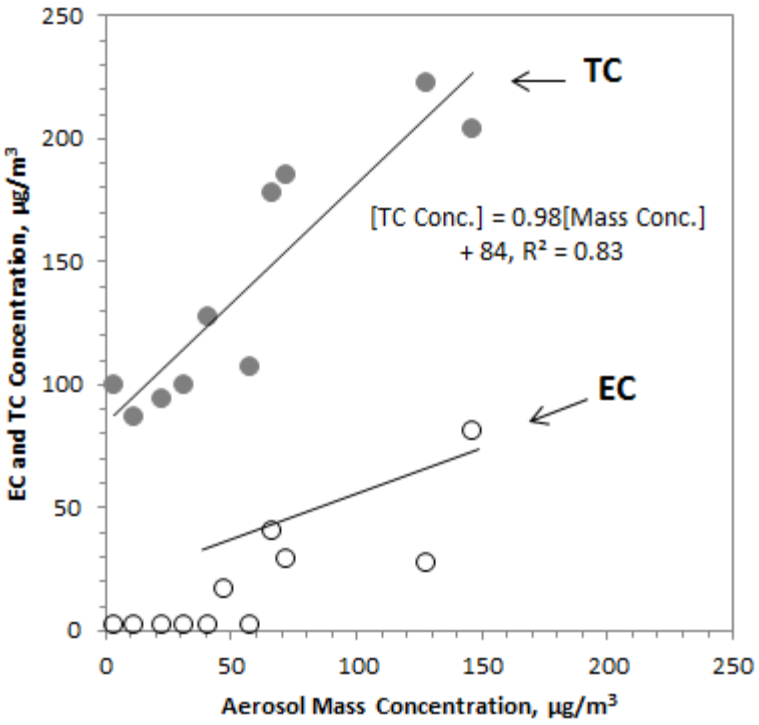

Figure 3. Aerosol mass concentration measured gravimetrically plotted against EC and TC concentration measured by Method 5040 for 95% MWCNTs.

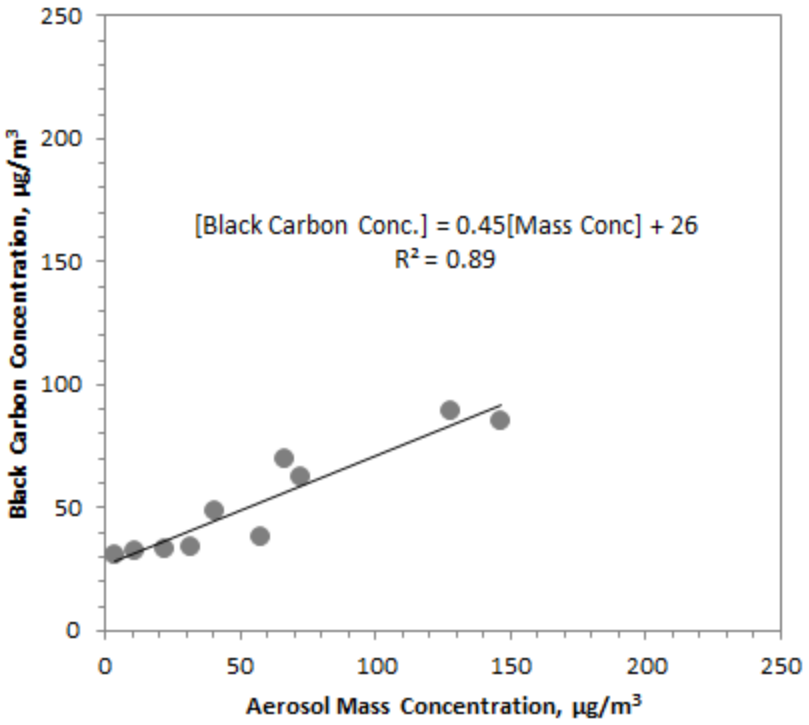

Figure 4. Aerosol mass concentration measured gravimetrically plotted against black carbon concentration measured by the aethalometer for 95% MWCNTs.

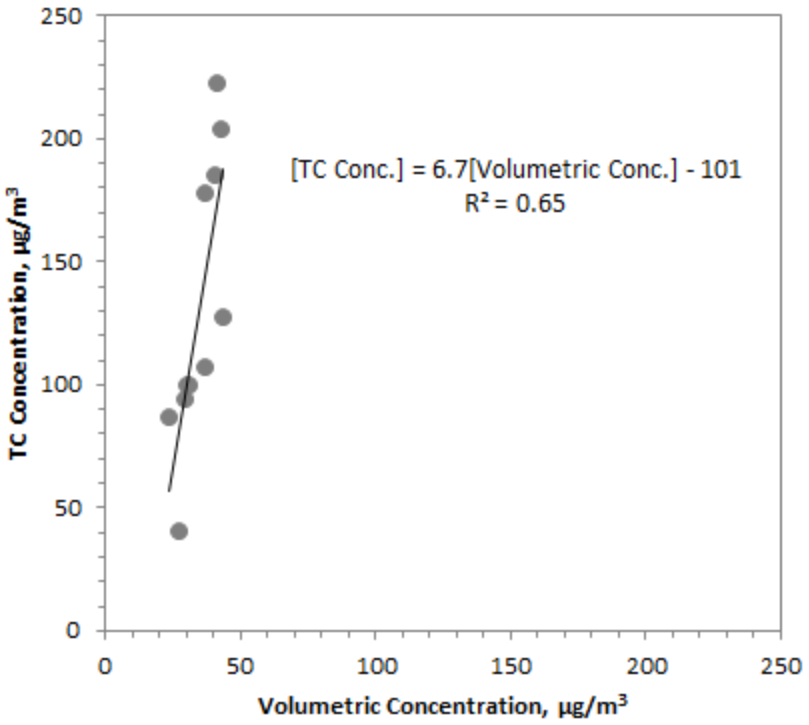

Figure 5. Volumetric concentration measured by SMPS plotted against TC concentration measured by Method 5040 for 95% MWCNTs.

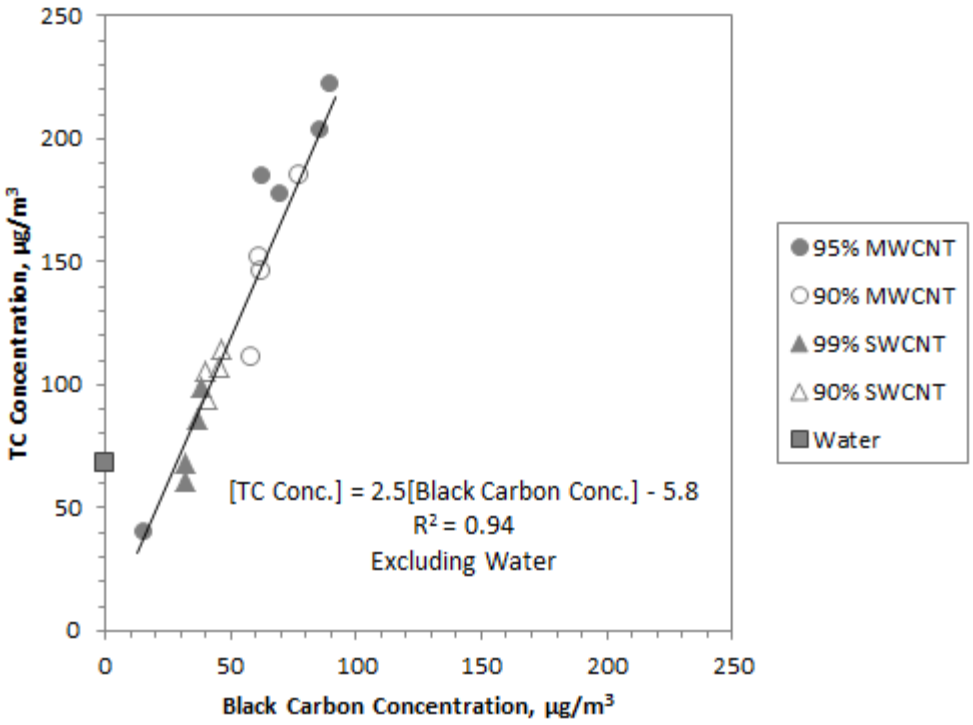

Figure 6. Black carbon concentration measured by the aethalometer plotted against TC concentration measured by Method 5040 among all CNT types and water-only sample.

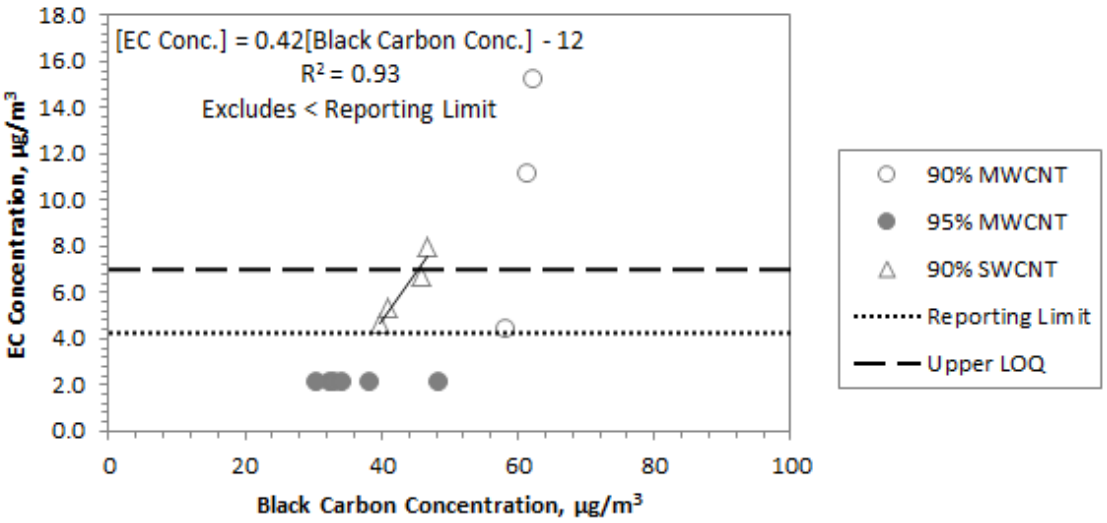

Figure 7. Black carbon concentration measured by the aethalometer and EC concentrations measured by Method 5040 showing a linear equation and R^2 value among several CNT types.

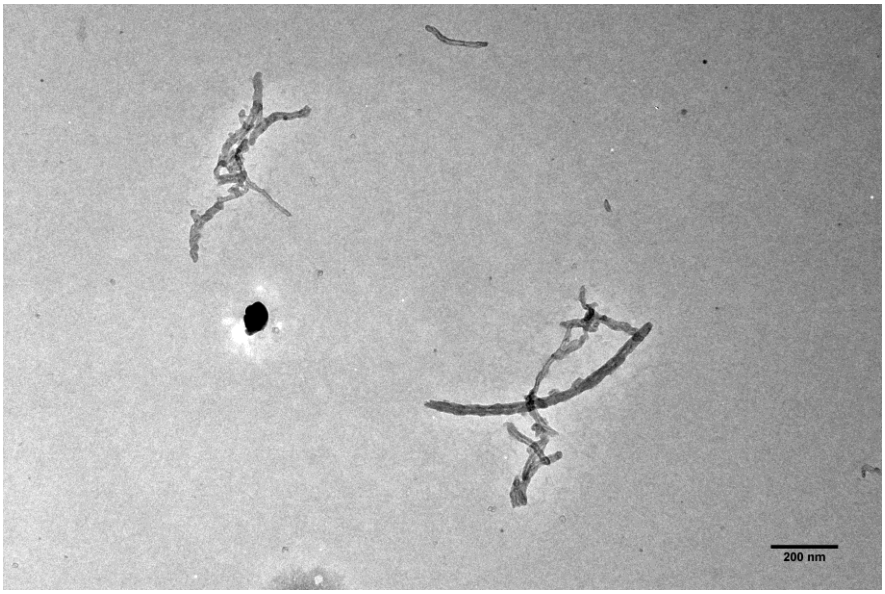

Figure 8. TEM analysis of 95% MWCNT sampled through the experimental apparatus.

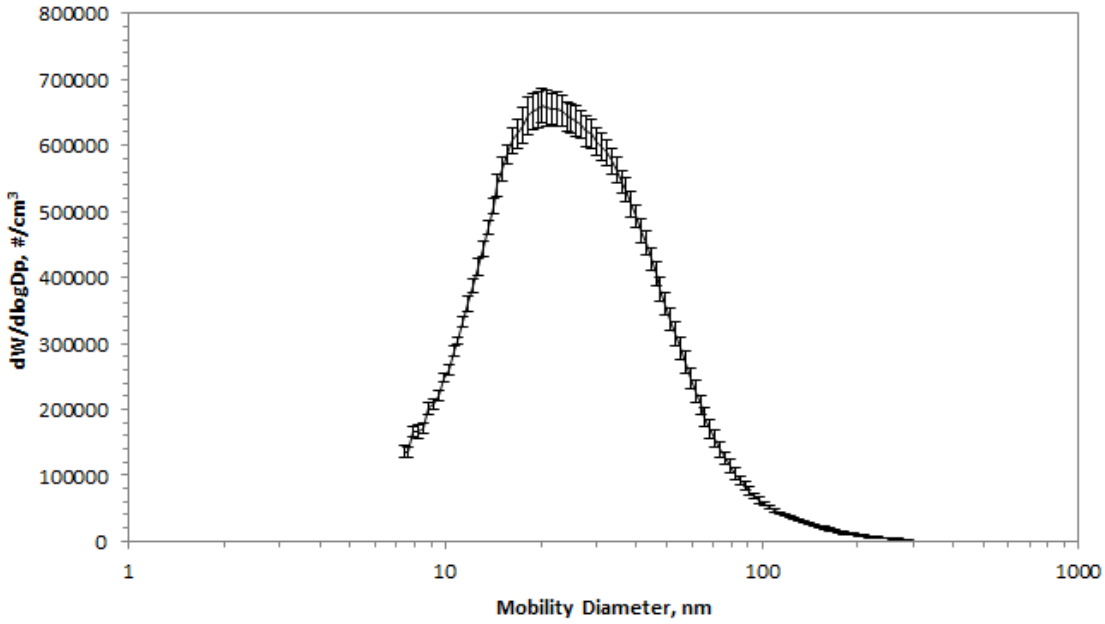

Figure 9. Normalized particle size distribution for 95% MWCNT samples with standard deviation.

CHAPTER III: CONCLUSIONS

In the field of industrial hygiene, conducting exposure assessments on CNTs may be a daunting task as nanotechnology is quickly advancing. Therefore the results of this study are especially applicable to those confronted with sampling and controlling CNT exposures in the workplace. If an industrial hygienist did have the need to quantify CNT exposures my initial recommendation would be to start with Method 5040 based on overall cost efficiency. The Method 5040 analysis amounted to $60 per sample and the total cost of the aethalometer and filter strips used in this study were $6,500, while the entire SMPS system was $65,000. Therefore, an investigator could have roughly 100 samples analyzed by Method 5040 before the overall expense neared the cost of the aethalometer. My recommendation would change, however if the sampling strategy were much more extensive, or if the investigator were interested in conducting exposure mapping over a large area. In such a case the aethalometer would be very useful because it averages exposure over a 5 minute period and can be used to identify tasks associated with high black carbon concentration and/or high CNT concentrations.

Another recommendation that I would make to the investigator would be to include a respirable sampling device, such as a cyclone, in their sampling strategy. By removing particles with diameters greater than 10 μm the remaining aerosol that reaches the aethalometer can be directly compared with the NIOSH CNT REL. Also, in order to ensure that the Method 5040 reporting limit was lower than the NIOSH REL for CNTs, a 25-mm cassette should be used at a higher flow rate.

The aethalometer used in this study was simple to use for area sampling, however on two occasions the aethalometer stopped working unexpectedly. For both occasions the instrument was taken apart and cleaned. Cleaning consisted of wiping the optic lens chamber of dust, however there was very little dust present. If the aethalometer were used

in a facility with large suspended particulate concentrations, cleaning and servicing the device may become an issue.

If this study were repeated in the future I would recommend that the investigator aim to produce samples near the upper LOQ of Method 5040 and if possible, to repeat several samples within the range of the reporting limit and the proposed NIOSH REL for CNTs. Additionally, I would recommend to heat-treat the quartz fiber filters prior to using them. I also would ensure that blanks were incorporated into the study, and also would analyze the bulk CNT samples to determine their EC carbon contents.

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