Final Report

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List Terms and Abbreviations

AFM	Atomic Force Microscopy
AP	As-produced grade
ARC	Arc Discharge
CNT	Carbon Nanotube
CPC	Condensation Particle Counter
CVD	Chemical Vapor Deposition
DMA	Differential Mobility Analyzer
DWCNT	Double-walled Carbon Nanotube
ELPI	Electrical Low Pressure Impactor
HiPCO	High-Pressure CO Conversion
HP	High-purity grade
ISDB	Integrating Screen Diffusion Battery
LPS	Laser Particle Spectrometer
MWCNT	Multi-walled Carbon Nanotube
PM	Particulate Matter
SWCNT	Single-walled Carbon Nanotube
WPS	Wide-range Particle Spectrometer

ABSTRACT

Carbon nanotubes (CNTs) are among the most dynamic and fast-growing engineered nanomaterials due to their novel properties. Now, they can be produced in bulk quantities by a number of established methods, such as, electric arc discharge, chemical vapor deposition, high pressure CO conversion, etc. Industrial scale production is expected in the near future. As production and application increase, the potential of human exposure to this new type material in the workplace as well as in the general environment are increasing, and their impacts on human health are of great concern by many researchers. There is a serious lack of information regarding the aerosol behavior and properties of such new and unique substances, as well as a lack of adequate detection and monitoring technologies.

CNTs are highly agglomerated and often coexist with non-tubular type particles, such as amorphous carbon soot, metal catalysts as well as ambient particles. To identify agglomerated CNT particles in the presence of other airborne particles, and quantifying the number concentrations of a specific sub-size fraction, we developed a method for sampling, quantification and characterization of CNT particles in air, utilizing a 13-stage Electrical Low Pressure Impactor (ELPI) in parallel with a 6-stage Integrating Screen Diffusion Battery (ISDB). The system is capable of monitoring particle concentration and size distribution real-time and collecting size segregated particle samples for detection and quantification of CNT contents in each size fraction by Atomic Force Microscopy (AFM) and automated image analysis software (SIMAGIS® Nanotube Solutions). By applying an appropriate deagglomeration pretreatment, the sampled particles can be classified into two categories: tubular (individual nanotubes and/or their agglomerates) and non-tubular (soot, dust, metal catalysts, and other co-existing nano-particles). Physical size and shape characters of tubular particles can also be determined with respect to the diameter, length, aspect ratio and curvatures, respectively.

The technology has been applied for monitoring and characterizing airborne unrefined CNT samples (raw materials). 7 industrial grade CNT samples of various types have been examined in this study, including single-walled, double-walled and multi-walled nanotubes. The experimental data demonstrated that all types of CNT raw materials examined can be dispersed into air to a significant extent with agitation. The sizes of particles generated were widely

distributed and varied with the type of CNTs and with the methods by which they were manufactured. By using a 6-stage ISDB, we have also resolved the particle size mode under 3 nm, a size range that is not quantifiable by other current particle instruments. By number counts, the majority particles are in the respirable-size region (< 4 μm) for all types of CNT samples examined in this study; implying that CNTs can possibly become airborne during manufacturing and handling processes and expose humans via inhalation or dermal absorption.

The image analysis results by AFM showed that the CNTs tend to agglomerate rather than to exist as single particles, physically. As deposition efficiency and sites of inhaled particles within the respiratory system largely depends on particle size distribution, the deposition pattern of agglomerated CNT should be similar to those equivalent sized non-agglomerated particles. Nevertheless, entrained particles depositing on/in the deep lung surfaces of the bronchioles or alveoli will contact pulmonary surfactants in the surface hypo phase and the agglomerated CNT are likely to be de-agglomerated. Therefore, to investigate human exposure to airborne CNTs, the characteristics of particles, such as, structure, size distribution and surface area, agglomeration state as well as purity of the samples, must be taken into account.

SECTION 1

1.1. Significant Finding

In this study, we developed following technologies for sampling, monitoring and characterizing airborne carbon nanotube (CNT) particles:

1) A system for monitoring airborne CNT particles by using an Electrical Low Pressure Impactor (ELPI) in parallel with an Integrating Screen Diffusion Battery (ISDB). The system is capable of collecting size segregated particle samples and monitoring particle concentration and size distribution of particles real-time in a wide size range from 10 micrometer down to single nanometer scale.
2) A method for detection and characterization of CNTs using AFM image analysis and automated image analysis software, SIMAGIS® Nanotube Solutions. The method is capable of identifying agglomerated CNT nanoparticles in the presence of other airborne particles. By applying an appropriate deagglomeration pretreatment, the sampled particles can be classified into two categories: tubular (individual nanotubes and/or their agglomerates) and non-tubular (soot, dust, metal catalysts, and other co-existing nano-particles). Physical size and shape characters of tubular particles can also be determined with respect to the diameter, length, aspect ratio and curvatures, respectively.

These technologies were applied to investigate the size distribution and characteristics of aerosol particles that were released from industrial grade unrefined CNT materials of various types including single-walled (SWCNT), double-walled (DWCNT) and multi-walled (MWCNT) nanotubes. The experimental results demonstrated that all types of unrefined CNT samples examined can be dispersed into air to a significant extent with agitation. The sizes of particles generated were widely distributed and varied with the type of CNTs and with the methods by which they were manufactured. By number counts, the majority particles are in the respirable-size region ($d_p \leq 4$ μm). The image analysis by AFM showed that the CNTs tend to form clusters rather than to exist as single particles, physically.

1.2 Translation of Finding

Carbon nanotubes are among the most dynamic and fast-growing engineered nanomaterials due to their novel properties. To assess the potential of human exposure to this new type material in the workplace as well as in the general environment, and their impacts on human health, in this study, we have developed a practicable sampling and image analysis method for detection and quantification of CNT aerosol particles that is not only capable of monitoring the particle size distribution for all particles, but also of distinguishing CNTs among other engineered and environmental particulate matter (PM), measuring number concentration and shape characteristics (diameter, length, aspect ratio, curvatures) of CNT particles in each aerodynamic size fraction, and hence an adequate technology for monitoring and characterizing airborne CNTs in workplace.

The experimental results of this study demonstrated that all types of unrefined CNT materials can be dispersed into air through agitation. Therefore, they could become airborne and expose workers through inhalation and dermal exposure during manufacturing and handling processes, and subsequently during product repair, replacement, or disposal.

Based on the experimental data, we also found that CNT particles tends to agglomerate rather than to exist as individual tubes. Sizes of dispersed CNT particles are widely distributed, and vary with the material types. By number counts, the majority particles are in the respirable-size region ($d_p \leq 4$ μm). As deposition efficiency and sites of inhaled particles within the respiratory system largely depends on size distribution, the deposition pattern of CNT agglomerates should be similar to those equivalent sized non-agglomerated particles. Nevertheless, entrained particles depositing on/in the deep lung surfaces of the bronchioles or alveoli will contact pulmonary surfactants in the surface hypo-phase and the agglomerated CNT are likely to be de-agglomerated. Available literature data based on the animal studies show that the discrete nanoparticles can enter the bloodstream from the lung and translocate into the systemic circulation and cause adverse health effects. Therefore, to investigate human exposure to airborne CNTs, the characteristics of particles, such as, structure, size distribution and surface area, agglomeration state as well as purity of the samples, must be taken into account.

1.3 Outcomes

Growing applications and mass production of Carbon nanotubes have raised concerns about their safety in the workplace as well as in the general environment. Our experiment results demonstrated that unrefined CNT materials can be dispersed into air to a significant extent with agitation. By number counts, the sizes of dispersed particles are mainly in the respirable-size region (< 4 μm); implying that CNTs can possibly become airborne during manufacturing, processing and handling of the materials and expose workers via inhalation or dermal absorption.

There is currently very limited knowledge regarding the human health, worker safety, or environmental impacts of this new type of material. Also there is a lack of adequate methods for detection and quantification of CNT particles in air. CNTs are highly agglomerated and often coexist with non-tubular type particles, such as amorphous carbon soot, metal catalysts as well as ambient PM. Though a variety of technologies and instruments are available for accurate measurement of overall concentration or size distribution of ultrafine and micron-sized particles, they are not capable of distinguishing engineered nanoparticles from other particles present in the same airspace. The method developed in this study, utilizing the technologies of ELPI/ISDB sampling and AFM image analysis, is able to monitor particle concentration and size distribution in real-time and collect size segregated particle samples for detection and quantification of CNT contents in each specific sub-size fraction. The method can identify CNT particles among other engineered and environmental PM and provide well-characterized CNT particle data (such as, structure, agglomeration state, concentration, and size distribution and surface area) that are needed for assessing potential worker exposure to airborne CNTs in an environment involves manufacturing, processing and handling of the raw materials. The technologies developed in this work also provide a foundation for further development of field and personal sampling devices for CNTs.

SECTION 2

2.1. Scientific Report

2.1.1. Background

Carbon nanotubes (CNTs) represent a new form of carbon that has closed tubular structures, consisting of nested cylindrical graphitic layers with a hollow internal cavity and capped by fullerene-like ends (Iijima 1991). There is a wide variety of CNTs, but they can be categorized into two classes: single-walled (one tube) or multi-walled (multiple concentric tubes) that are commonly abbreviated to SWCNTs and MWCNTs, respectively. CNTs have great tensile strength and are considered to be 100 times stronger than steel, but only about 15% of its weight, making them potentially the strongest, smallest, lightest fiber known. CNTs also have numerous unique physical and chemical properties, such as, high conductivity, high surface area, unique electronic properties and potentially high molecular adsorption capacity, making them potentially useful in a wide range of applications, such as, polymer composites (conductive and structural filler), electromagnetic shielding, electron field emitters (flat panel displays), super capacitors, batteries, hydrogen storage and structural composites, as well as cancel therapy and drug delivery systems. Over the past two decades, CNTs have received enormous attention from researchers all over the world to explore their potential applications and techniques for mass production. Now, they can be produced in bulk quantities by a number of established methods, such as, electric arc discharge, chemical vapor deposition (CVD) and high pressure CO conversion (HipCO), etc. As production rate scaling up, the potential of human exposure to this new material in workplaces as well as in general environments are increasing and their potential impacts on human health are of concern by many researchers (Colvin 2003; Dagani 2003, Lam et al. 2004, Shvedova, et al. 2003 and 2005, Warheit et al. 2004). The experimental data from several studies demonstrated that with an equivalent mass dose, CNT particles have more adverse effects on rats than other nano-sized (< 100 nm) particles, such as, carbon black and quartz particles. Based on the experimental results on mice, Shvedova et al. (2005) estimated that workers may be at risk of developing lung lesions if they were actually exposed to SWCNT over a period of 20 days at the current OSHA Permissible Exposure Limit (PEL) for synthetic graphite (15 mg/m^3 of total dust or 5 mg/m^3 of respirable fraction) as stated on current Material

Safety Data Sheet (MSDS) of the CNTs. Lam et al. (2004) provided similar estimations and suggested that the graphite PEL should not be used as a safe concentration for workers exposed to CNTs. Like graphite and carbon black, CNTs are formed from carbon atoms. However, their special long-winded fibrous structure offers unique surface chemistry and distinguishing physicochemical properties. These characteristics may possibly affect their toxicity in humans. The coexisting metal nanoparticles (as catalysts of CNT production) may also be a contributing factor for the development of adverse responses.

The diameters of individual CNTs range from 1 - 2 nm for SWCNTs to tens of nm for MWCNTs, but their lengths are commonly a few to hundreds of micrometers, and aspect ratio (a ratio of length to diameter) is typically about 10^2 but can reach as high as 10^4. For fiber-like particles (those with high aspect ratios), particle shape is also an important parameter. CNTs resemble asbestos fibers in terms of aspect ratio (long and needle-like), but they tend to clump together rather than exist as single high aspect ratio particles. However, in order to make this material more commercially useful, intensive research is already underway to de-clump the ropes into single detached fibers. Based on the experimental results, Muller et al. (2005) suggested that the potential exposure and health risks of inhaled nanofibers may not be dissociated from the well-known adverse effects of asbestos fibers, although a fiber effect would only be expected if the nanotube encounters an appropriately sized cellular structure, analogous to the asbestos fiber/macrophage relationship. Whether the behavior and toxicity of CNT particles is similar to other ultrafine particles or fibers, and whether it is possible to extrapolate from the existing toxicological data base on ultrafine particles and fibers, remains uncertain and needs to be determined.

To determine the overall risk to humans, not only the toxicity but also the exposure levels need to be considered. Studies have shown that worker exposure by mass to respirable-sized CNTs would be low (ranging from not detectable to below 0.1 mg/m^3) (Baron et al. 2002; Joseph 2002; Maynard et al. 2004). Nonetheless, given the unusual toxicity of CNTs observed in rodent lungs at relatively low mass doses, even these small exposures may not be negligible. Also, these exposures were evaluated on a mass concentration basis (mass per unit volume). To evaluate low-solubility nano-sized particles, number concentration, or surface area, may be a more relevant exposure parameter (Oberdörster et al., 2004). Caution should remain until more conclusive toxicity data are achieved, and it will be important to record appropriate measures of worker exposure for retroactive risk assessment.

There is a serious lack of information regarding the aerosol behavior and properties of such new and unique substances, as well as a lack of adequate detection and monitoring technologies. Therefore, practicable sampling technologies as well as methods for detection and quantification of CNT aerosol particles are urgently needed.

2.1.2. Specific Aims

The objective of this research is to develop a method for sampling, quantifying and characterizing airborne CNT particles, with respect to: their form, number concentration, size, shape and state of agglomeration. The method will be capable of identifying agglomerated CNT particles in the presence of other airborne particles, and can be used to measure size-resolved number concentrations of a specific sub-size fraction. The specific aims are to:

- Build an air monitoring system that is capable of real-time sampling and sizing airborne CNT particles in a wide size range by using an Electrical Low Pressure Impactor (ELPI);
- Explore other potential CNT sampling methods, such as an Integrated Screen Diffusion Battery (ISDB) previously developed in this laboratory; and
- Develop and test a practical method for quantification and characterization of CNT samples using Atomic Force Microscopy (AFM) and an automated SIMAGIS® imaging analysis software.

2.1.3. Methodology

Material Sources

Unrefined bulk CNT materials of as-produced (AP) grade or high-purity grade (HP) of different types were purchased directly from the manufacturers. The data of average bundle dimension and purity of each material are provided by individual manufacturers.

Test Aerosol Generation

The test aerosols were laboratory generated from industrial grade bulk materials through agitation. CNT raw material were placed in a vertical cylinder (2.5 cm in diameter and 8 cm in length) and agitated by a vortex agitator with low to medium power. Aerosol particles were released from the bulk material and carried out of the generator by a low dispersion air flow (0.25 liter/min). The aerosol flow was then mixed with a dilution air flow (20 liter/min) prior to entering the monitoring system as illustrated in Figure 1. To eliminate transport losses, aerosol generated were charge-neutralized by a neutralizer containing Po-210 sources. HEPA filtered air was used for both dispersion and dilution air in order to produce the 'pure' CNT aerosols.

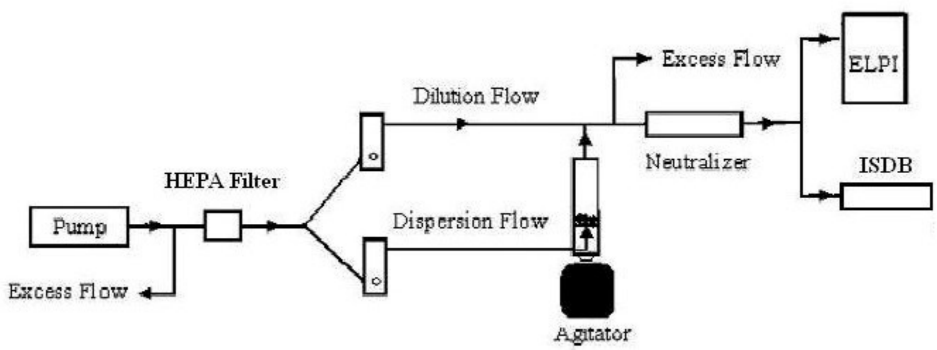


Figure 1. Schematic diagram of CNT aerosol generation and sampling system.

Sampling and Sizing Airborne CNT Particles

A system has been built in this work for measurement and characterization of CNT particles that are laboratory generated from industrial grade CNT bulk materials. A 13-stage ELPI (Dekati, Finland) and a portable 6-stage ISDB were connected in parallel for sampling and sizing airborne CNT particles.

1) *Electric Low Pressure Impactor (ELPI)*

ELPI is a real-time particle size spectrometer that consists of an aerosol charger and a cascade impactor. The particles are charged in a corona charger prior to entering the impactor. The aerosol particles are then size classified and collected onto the aluminum substrates placed on each stage except the filter stage, based on inertial impaction. The number concentrations of the particles collected onto the individual stages (electrically-insulated impaction plates) are determined by measuring the current carried by these particles using sensitive electrometers (in fA ranges). The ELPI measures a wide range of airborne particle size from 10 μm down to 30 nm. The range can be extended down to 7 nm with a filter stage in place. The cut-off sizes of each impactor stage are listed in Table 1. ELPI was used in this study for monitoring number concentration and number-weighted particle aerodynamic size distribution and collecting size segregated samples for detection and quantification of CNT contents in each size fraction by AFM.

Table 1. Calibrated aerodynamic cut-off size of ELPI.

Stage Number	**Aerodynamic Cut-size (μm)**
Filter	0.007
1	0.029
2	0.056
3	0.093
4	0.157
5	0.265
6	0.385
7	0.619
8	0.956
9	1.61
10	2.41
11	4.03
12	-
13	9.99

The performance of the ELPI sampling system was evaluated by inter-instrument data comparison with a Wide-range Particle Spectrometer (WPS-1000s, MSP, MN). WPS is also a real-time particle monitoring system, which features an integrated design of a scanning mode Differential Mobility Analyzer (DMA), a Condensation Particle Counter (CPC), and a Laser Particle Spectrometer (LPS) system. The test results showed that the particle number concentration and the number-weighted size distribution measured by the ELPI agreed well with those measured by WPS for mono-dispersed NaCl particles and polystyrene uniform microsphere (Duke Scientific, CA) in the size range of below 10 μm.

2) Integrating Screen Diffusion Battery (ISDB)

A portable ISDB was used in this study to collect particles and determine the size distribution of the nanometer-sized particles in the region below 30 nm. The device was previously developed and validated at our laboratory by Dr. Heikkinen, a former faculty member of NYU-SOM, for the collection of time-integrated samples of nanoscale particles (Heikkinen 1997). Figure 2 is a picture of two versions of the devices, the tubes and parts at the top and bottom are the components of a full version ISDB and the center parts are belong to a 6-stage mini-version. The 6-stage ISDB consists of a cylindrical aluminum tube with a 2-cm diameter and a set of 5 stainless steel wire screens with mesh sizes of 440, 375, 225, 100, and 60, respectively. The performance of this device is based on diffusional collection of nano-sized particles on the screens and walls of a round tube. On the walls of the tube, between the screens there are recessed slots for duplicate detectors (sample collectors). In this study, freshly peeled mica substrates (free of particle background) were used as detectors.


Figure 2. Photo pictures of Integrated Screen Diffusion Batteries (ISDB)

When the particles are sampled into the tube the smallest particles, with highest diffusion coefficients, are collected first. An increasing number of bigger particles are collected by the subsequent screens. The smaller the particles the more efficient the deposition on the tube wall and substrates will be. The particle size dependent deposition efficiency on the wall, η_D can be calculated with an equation derived by Ingham (1975) for predicting particle deposition by diffusion in developing flow condition:

$$\eta_D = 1.709\, I(\xi)\, \mathrm{Sc}^{-2/3}$$

$$I(\xi) = \int_0^{\xi} \frac{\sqrt{\Phi(\xi)}d\xi}{(\int_0^{\xi}\sqrt{\Phi(\xi)}d\xi)^{1/3}}$$

$$\xi = \frac{z}{R\,\mathrm{Re}} = \text{dimensionless entry length}$$

Where, $\Phi(\xi)$ is the wall surface friction, ν the kinematic viscosity, z the entrance length, R the tube radius, Re the Reynolds number = $2Q/\pi R\nu$, Q the flowrate, Sc the Schmidt number = ν/D, and D the diffusion coefficient of the particle.

The collection efficiency of each wire screen can be calculated using the equations presented by Cheng et al. (Cheng and Yeh 1980, Cheng et al. 1980, 1985):

$$E = 1 - \exp\{-4\alpha h n \eta / (\pi(1-\alpha) d_w)\}$$

Where, α is the solid volume fraction of the screen, h the thickness of the screen, n the number of screens, and d_w the screen wire diameter. The α, h, and d_w have already been determined for the screens in use. η is the single fiber efficiency and is defined as:

$$\eta = 2.7Pe^{-2/3} + (2\kappa)^{-1} f(R) + (2\kappa)^{-2} I\, Stk + 1.24\kappa^{-1/2} Pe^{-1/2} R^{2/3}$$

where Pe is the Peclet number = Ud_w/D, U the superficial flow velocity, D the diffusion coefficient of the particle, R the interception parameter = d_p/d_w, d_p is the particle diameter, η_a is the viscosity of air, and

$$f(R) = (1+R)^{-1} - (1+R) + 2(1+R)\ln(1+R)$$

$$\kappa = -0.5\ln(2\alpha/\pi) + 2\alpha/\pi - 0.75 - 0.25(2\alpha/\pi)^2$$

$$I = (29.6 - 28\alpha^{0.62}) R^2 - 27.5R^{2.8}$$

$$Stk = \rho_p C_c d_p^2 U / (9\,\eta_a d_w) = \text{the Stokes number.}$$

A computer program was used for calculation of the overall collection efficiencies of the substrates for particles with different diameters.

Particle samples collected on mica substrates placed on the tube wall were analyzed and counted for particle number concentration by AFM without pretreatment. Particle samples collected on the screens were used for topographic analysis with AFM to distinguish and separately quantify the tubes, ropes and non-tubular particles after being dissolved and deagglomerated by a surfactant and sonication.

Image Analysis by Atomic Force Microscopy (AFM)

An Atomic Force Microscope (AutoProbe CP-II, Veeco Instruments, Sunnyvale, CA) was employed in this work for measurement and characterization of CNT particles. AFM provides three-dimensional surface topography at nanometer lateral and sub-angstrom vertical resolution on either insulated or conducted samples by scanning a sharp oscillating probe tip mounted on the end of a flexible cantilever across a sample surface while monitoring the tip-sample interaction to form a high resolution image. Unlike SEM and other current technology for CNT measurement, the AFM is able to measure in all three dimensions (x, y, and z) with a single scan. AFM is superior to TEM & SEM for such applications, because it is relatively inexpensive and can be performed at ambient pressure.

The particle samples collected on the mica discs were scanned topographically by AFM using the non-contact mode. Non-contact AFM is one of several vibrating cantilever techniques in which the cantilever is vibrated near the surface of the sample. The space between the tip and the sample is on the order of tens to hundreds of angstroms; in the range of attractive van der Waals forces. The color scale on the AFM scans reflects the surface topography. The surface roughness (an AFM scan parameter) of blank mica substrates were used in judging the integrity of the substrates. Collected particles were sized and counted by scanning at least 4 randomly selected fields on each substrate. Because of the enormous counting effort required for these experiments, the following counting protocols were chosen in this study: At least 4 scans were done (one in each quadrant of the substrate) with a scan area of 100 μm^2 for each scan and a minimum total particle count of 200 detected in 4 scan areas. A count of 200 particles results in a Poisson counting error of 7%, which is acceptable. For non-tubular shaped particle samples with lower particle counts, larger areas up to 10,000 μm^2 were used in order to exceed the 200-count limit. For samples of tubular particles with diameter of only a few nanometers, the scan area could not be beyond 100 μm^2 because of the resolution of the instrument. Therefore, for those low counts samples containing tubular particles, 8-16 scans (total area of 800-1,600 μm^2), 2-4 in each quadrant, were counted. For quality control, a 5-µm calibration grating with 100nm×100nm pits were scanned periodically over the duration of the experiments to assure image integrity.

Data Analysis Module and Program for Nanotubes

Microscopic methods require observing many different tubes, one-at-a-time, and building a statistical histogram, which makes the approach time-consuming. SIMAGIS® Research software (Smart Imaging Technology, Inc. TX) is an image analysis and data processing program for micro as well as macro objects. The program includes a variety of automated functions for measurement and statistical analysis of the input image. An advanced Nanotube analysis module, SIMAGIS® Nanotube Solutions, was specifically designed for the applications with images from AFM, and can separately count tubes, ropes and non-tubular particles; measure shape characters including length, height, aspect ratio, curvature, and determine diameters for tubular particles.

2.1.4. Results and Discussion

CNTs are highly agglomerated and often coexist with non-tubular type particles, such as amorphous carbon soot, metal catalysts as well as ambient PM. To identify agglomerated CNT particles in the presence of other airborne particles, and further to quantify the size-resolved number concentrations of a specific sub-size fraction, we developed a method that utilizes a 13-stage ELPI combined with image analysis by Atomic Force Microscopy. The technology was applied in this study for monitoring and characterizing airborne CNT particles that were generated from unrefined bulk materials. 7 industrial grade bulk material samples from 3 manufacturers have been tested. The sample matrix includes all 3 common types of CNTs, i.e., single-walled (SWCNT), double-walled (DWCNT) and multi-walled (MWCNT), and 3 primary manufacturing methods, i.e., arc discharge (Arc), chemical vapor deposition (CVD), and high-pressure CO conversion (HiPco). The experimental results showed that all types of unrefined CNT samples can be dispersed into air to a significant extent (about 30-60% by weight) under medium power of agitation and with a dispersion air flow of as low as 0.25 liter/min. The flowrate of dispersion air was set at 0.25 liter/min (equivalent to an air velocity of 0.01 m/s) for mimicking a calm workplace air condition.

Number-Weighted Size Distributions of Various Types of CNT

The number-weighted size distribution of CNT aerosols were monitored by ELPI. Table 2 and Figure 3 show a set of ELPI measurement results for the number-weighted aerodynamic size distribution of particles released from various types of CNTs. The experiment results demonstrated that:

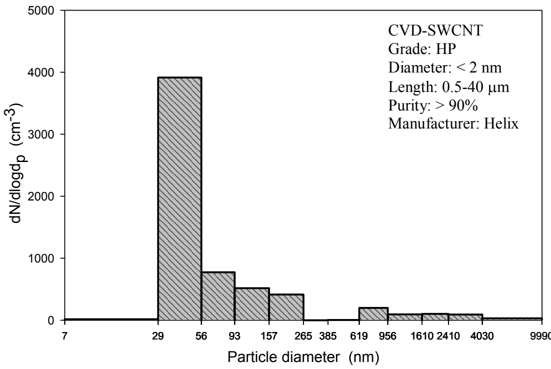
1) Airborne unrefined CNT aerosol particles are highly agglomerated. The particle sizes generated from all types of CNTs examined were widely distributed across all 13 stages of the ELPI including the filter stage. Thus, particles detected range from 7 nm to 10 μm in diameter.
2) The size distributions of dispersed particles varied with the type of CNTs and with the methods by which they were manufactured.
3) By number counts, the majority particles are in the respirable-size region (< 4 μm) for all types of CNT samples examined in this study.

The number-weighted nano-size fraction ($d_p \leq 100$ nm) of dispersed particles is correlated with the average dimension of individual tubes, especially the diameter as shown in Table 2 (except Hipco-SWCNT). For example, for the nanotubes produced by CVD method, the size of dispersed particles of MWCNTs (~10nm in diameter) tends to be larger than DWCNTs (~5nm in diameter) and much larger than SWCNTs (1.2 - 1.5nm in diameter).

Table 2. Number-weighted nano-size fraction of airborne aerosol particles released from various types of unrefined CNT materials due to agitation.

CNT Type	Grade	Production Method	Manufacturer	Carbonaceous Purity	Original Bundle Dimension		Number-weighted Nano-Size Fraction (dp ≤ 100 nm)
					Diameter (nm)	Length (μm)	
Single-walled	HP	CVD	HELIX Richardson, TX	> 90%	< 2	0.5 - 40	80%
Single-walled	AP	Arc	Carbolex Inc Indianapolis, IN	50-70%	1.4	2 - 5	35%
Single-walled	AP	CVD	HELIX Richardson, TX	50-70%	1.2 - 1.5	0.5 - 3	30%
Single-walled	AP	HiPco	CNI Houston, TX	> 65%	0.8 - 1.2	0.1 - 1	3%
Double-walled	HP	CVD	HELIX Richardson, TX	90%	< 5	0.5 - 40	20%
Multi-walled	Short	CVD	HELIX Richardson, TX	95%	< 10	1 - 2	5%
Multi-walled	Standard	CVD	HELIX Richardson, TX	95%	< 10	0.5 - 40	1%

(a)



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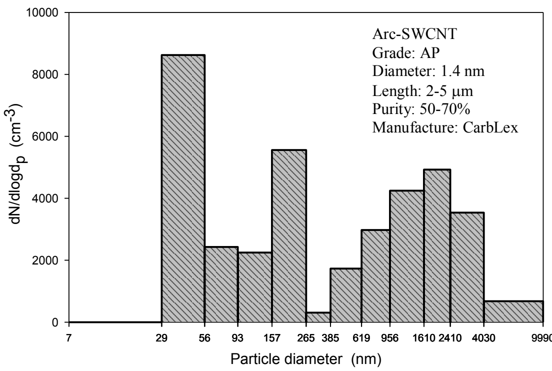

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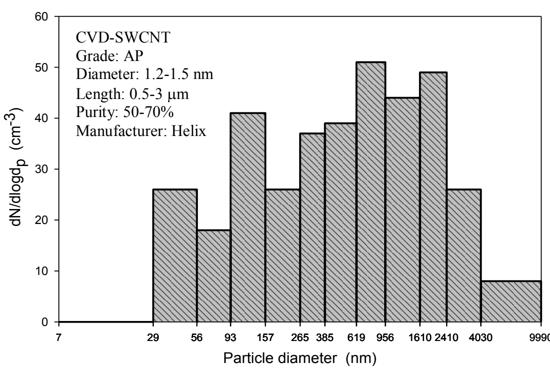

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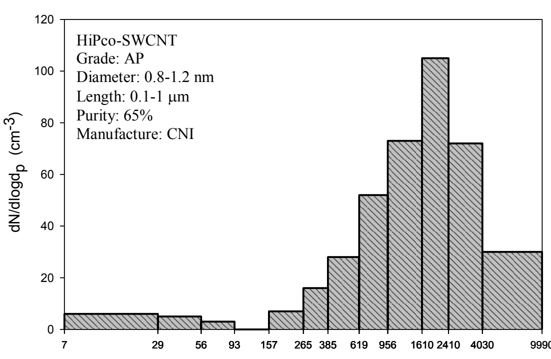

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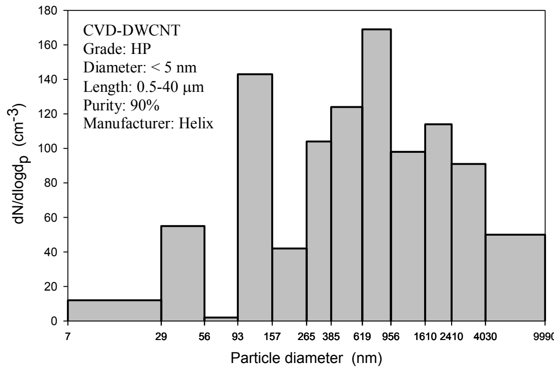

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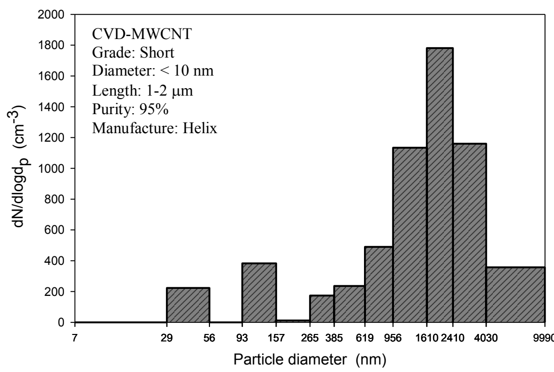


(g)

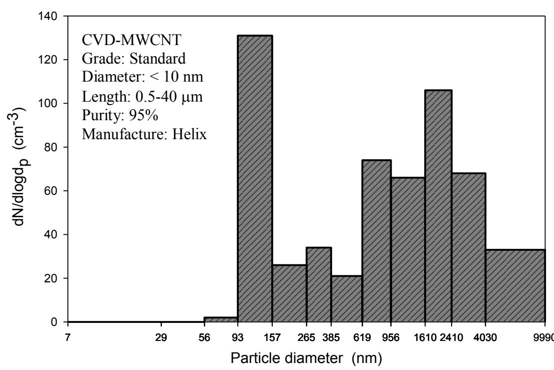


Figure 3. Number-weighted size distribution of various types of CNTs: (a) HP-grade CVD-SWCNT (Helix, TX); (b) AP-grade Arc-SWCNT (CarboLex, IN); (c) AP-grade CVD-SWCNT (Helix, TX); (d) AP-grade HiPco-SWCNT (Carbon Nanotech Institution, Houston, TX); (e) HP-grade CVD-DWCNT (Helix, TX); (f) Short CVD-MWCNT (Helix, TX); and (g) Standard CVD-MWCNT (Helix, TX).

Size Distribution of CVD-SWCNT in Nano-region

To extend the ELPI measurement to the true nano region (under 10 nm), Integrating Screen Diffusion Battery technology was employed in this work.

The CNT samples collected on the mica disc detectors placed on the walls of each stages of ISDB were analyzed (without deagglomeration treatment) by AFM to measure the number density on each substrate. A sample set of AFM images of CVD-SWCNT aerosol (HP grade, Helix, TX) collected on the walls of each stage of a 6-stage ISDB are shown in Figure 4. Each image represents one AFM scan result for one stage sample. To assure accurate measurement, typically, a set of 4 – 16 scans were performed for each stage sample. The statistical results of measured particle number counts on each stage of the sample set are shown in Table 3.

An Extreme Value Estimation (EVE) data deconvolution program (Tapper, et al. 1990, Paatero 1990) was used to obtain a number-weighted size distribution of CNT aerosol samples sampled by ISDB. In the EVE approach, first an optimum solution to the experimental data is sought by minimizing the sum of squares of the weighted residuals and then all the acceptable solutions are determined within a predetermined confidence interval. The confidence interval used in this work is about 95% which corresponds to about twice standard deviation. In the two-stage modeling used by EVE the original unknown function (distribution) is represented as a superposition of an arbitrary number of smooth basis curves, e.g. log-normal distributions. This introduces smoothing in the solution, in addition to the non-negativity restriction, and estimation of extreme values and smooth functions. A computer program previously established in this laboratory was used for calculation of the overall collection efficiencies of the substrates and screens for particles with different diameters.

Figure 5 shows the number-weighted size distribution of the above CVD-SWCNT aerosol sample calculated by the EVE data deconvolution program based on the statistical data set listed in Table 3. A significant fraction of particle number counts was found in the size region below 10 nm with a mode of 2.24-2.4 nm and GSD of 1.22-1.24. There is another peak in larger sizes, but it cannot be resolved based on this data set.

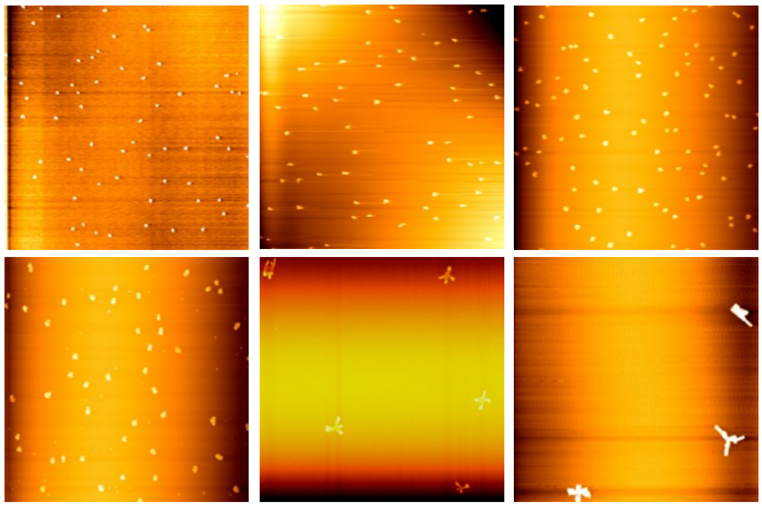


Figure 4. AFM Images gallery of a CVD-SWCNT particle sample collected on the walls of each stage of a 6-stage ISDB (Non-contact mode: scan size: 25μm×25μm). Top row left to right: stages 1-3; and bottom row left to right: stages 4-6, respectively.

Table 3. Counts of particles collected on the walls of each ISDB stage for an aerosol of CVD-SWCNT (high purity Grade, Helix, TX).

Stages	Particle Counts/10000μm^2	
	Mean	s.d
1	1120	242
2	1584	156
3	1520	171
4	1000	102
5	76	7
6	46	13

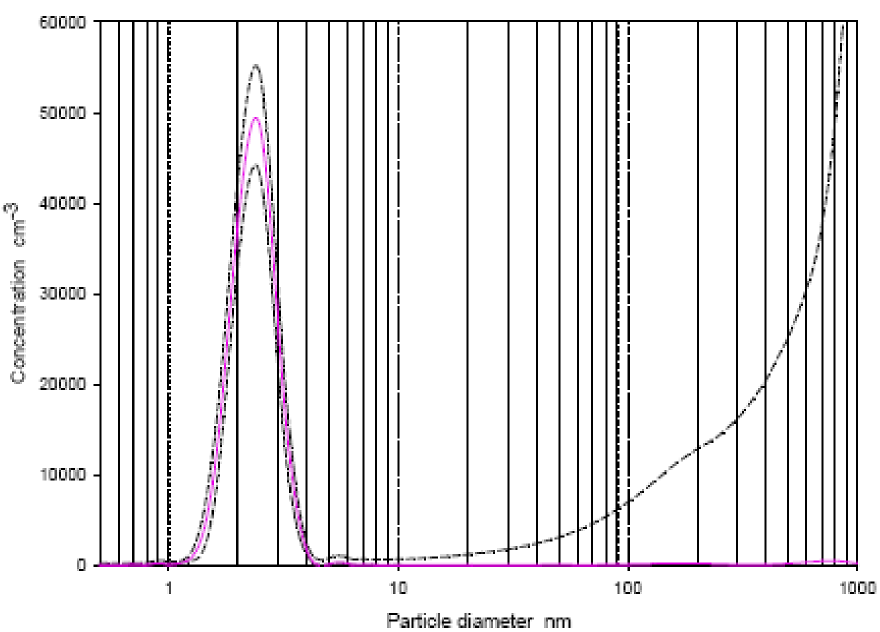


Figure 5. Number-weighted size distribution of aCVD-SWCNT aerosol sampled by ISDB. The data were calculated using the EVE program with a 95% confidential level.

These AFM images and experiment results clearly demonstrate that:

1) The CNT particles dispersed into the air are highly agglomerated, no single nanotubes

were found in all ISDB stages.

2) The particles collected on the mica discs are quite uniformly distributed. Therefore, particle size distributions sampled by ISDB can be calculated based on the total particle number counts collected on each stage using the EVE data deconvolution program.
3) The experiment results demonstrate the capability of a mini-ISDB for sampling and characterization of the CNT particles in the single nanometer region, a size range that is not quantifiable by other current particle instruments.

Particle Morphology

AFM results showed that all generated unrefined CNT aerosol particles are highly agglomerated; no single tubes or simple ropes were found in the samples collected on the stages of the ELPI or ISDB before sample treatment with surfactant. The agglomeration status of CNTs makes accurate quantification and characterization of the samples by AFM image analysis difficult. An effort was made to find an effective method for sample deagglomeration treatment. Dimethylformamide (DMF) was found one of the effective surfactants for CNT deagglomeration.

Figure 6 demonstrates two AFM images of a DMF-treated particle sample of CVD-SWCNT (HP grade, Helix, TX) on a mica disc. Its precursor was collected on ISDB Screen-stage 3 (mesh 200). The screen sample was then dissolved and deagglomerated by 1.5 ml DMF solution with 25 minutes sonication in an ice cooling bath. 1 µl resulting solution was plated onto a freshly peeled particle-free mica disc and baked for 90 minutes in a vacuum oven (200 ^{0}F and 125 mmHg). Collected particles on the mica surface were scanned topographically by AFM using the non-contact mode. The surface roughness (an AFM scan parameter) of blank substrates was used in judging the integrity of the substrates.

Figure 7 demonstrate an AFM image of a 29 µg/ml of CVD-SWCNT (HP grade, Helix, TX) raw sample deagglomerated by DMF with 5 minutes sonication. The result of image analysis by SIMAGIS® Nanotube Solutions is shown in Figure 8.

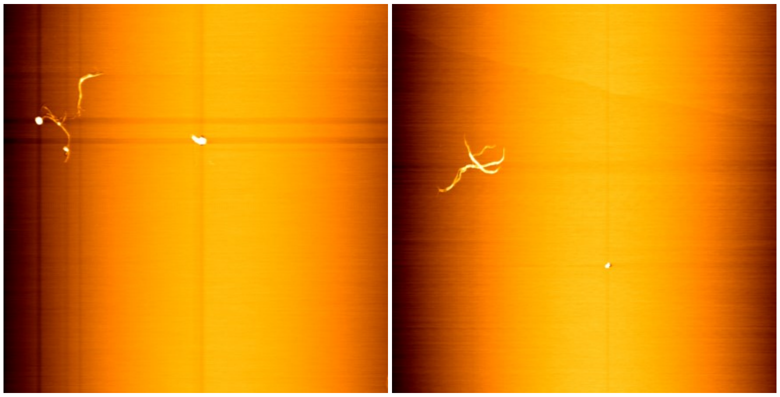
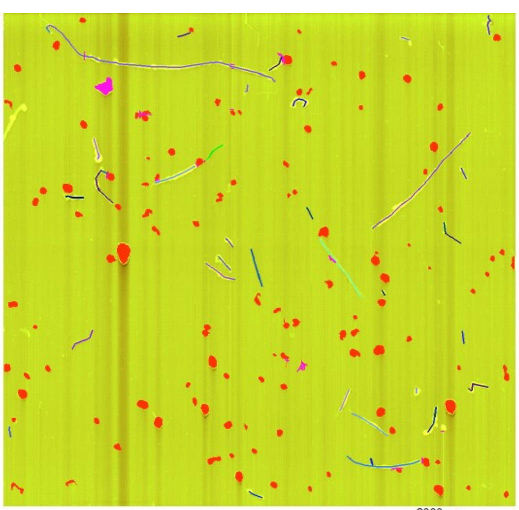


Figure 6. Particles of CVD-SWCNT (HP grade, Helix, TX) collected on ISDB Screen-stage 3 (mesh 200). The sample was dissolved and deagglomerated by DMF with 25 minutes sonication [Scan size: 5μm x 5μm].

Figure 7. An AFM image of a 29 μg/ml CVD-SWCNT (HP grade, Helix, TX) sample deagglomerated by DMF with 5 minutes sonication [Scan size: 10μm x 10μm].



Carbon Nanotubes Analysis

File: 0801P00b.hdf

Tube analysis results				
Number of tubes	2			
Statistics	Length,nm	Height,nm	H/L ratio	Curvature
Minimum	453	1	0.0007	0.04
Maximum	1469	1	0.0033	0.10
Average	961	1	0.0020	0.07
Median	1469	1	0.0033	0.10
Standard deviation	718	0	0.0018	0.04

Rope analysis results				
Number of ropes	35			
Statistics	Length,nm	Height,nm	H/L ratio	Curvature
Minimum	98	3	0.001	0.00
Maximum	4975	15	0.138	0.53
Average	592	7	0.026	0.07
Median	352	7	0.019	0.03
Standard deviation	905	3	0.025	0.11

Particle analysis results				
Number of particles	127			
Statistics	Length,	Height,nm	H/L ratio	Curvature
Minimum	--	-0.6	--	--
Maximum	--	121.6	--	--
Average	--	17.9	--	--
Median	--	13.0	--	--
Standard deviation	--	16.2	--	--

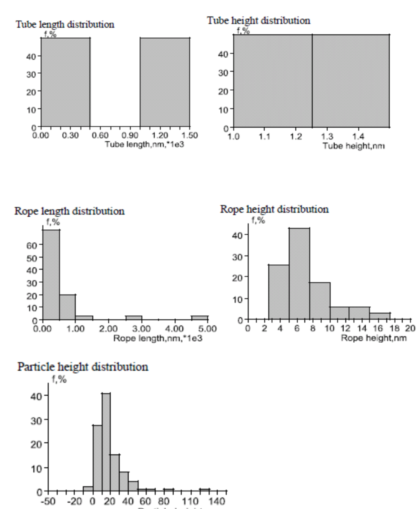
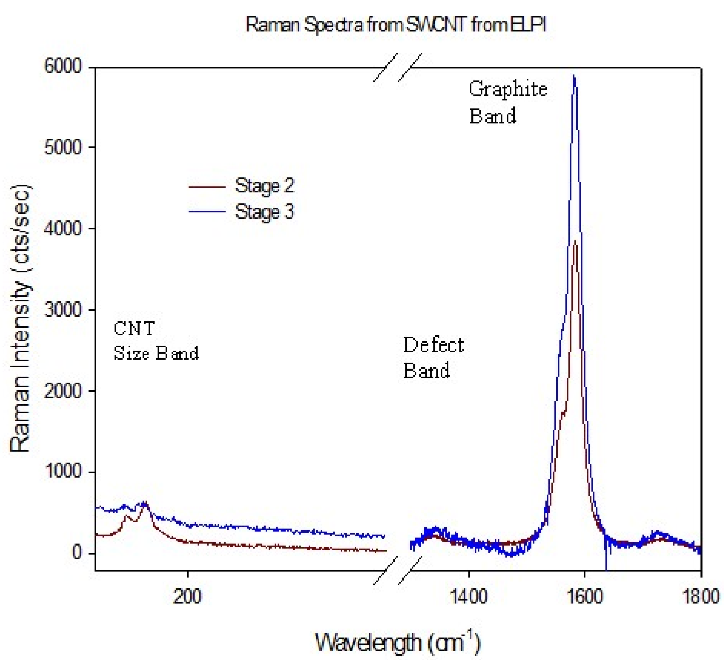


Figure 8. An analysis result for AFM image as shown in Figure 7 with SIMAGIS® Nanotube Solutions software.

Sample prescreening

In effort to reduce the elaborate AFM image analysis task, Dr. Xiong teamed with Dr. Madalina Chirila, a NIOSH scientist at Exposure Assessment Branch, Morgantown, WV to develop a CNT sample pre-screening technique to opt out the air samples that do not contain CNTs by utilizing Raman spectroscopy. Raman spectra directly reflect the chemical composition and the molecular structures. Carbon nanotubes are structurally related to graphitic carbon. There are three feature bands of the Raman spectrum from carbon nanotubes: the radial breathing mode (RBM) around 200 cm^{-1}, Defect band around 1350 cm^{-1}, and the Graphite bands around 1580 cm^{-1}. These bands are unique to the nanotubes, and hence can be used for identifying the nanotube contents from other chemical substance including non-tubular carbonaceous materials. Raman is a relatively fast, low-cost and non-destructive testing technology and therefore a practical method for CNT sample prescreening.



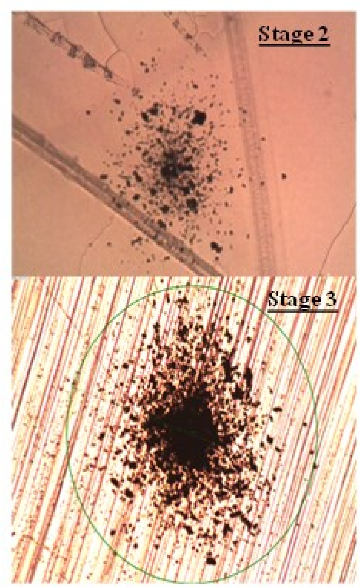
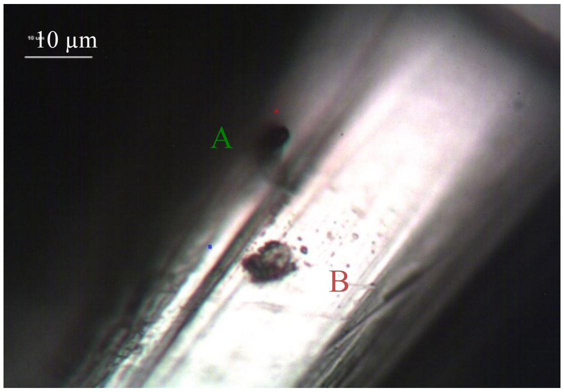


Figure 9. Raman Spectra of a CNT sample collected on Stages 2 and 3 of ELPI.



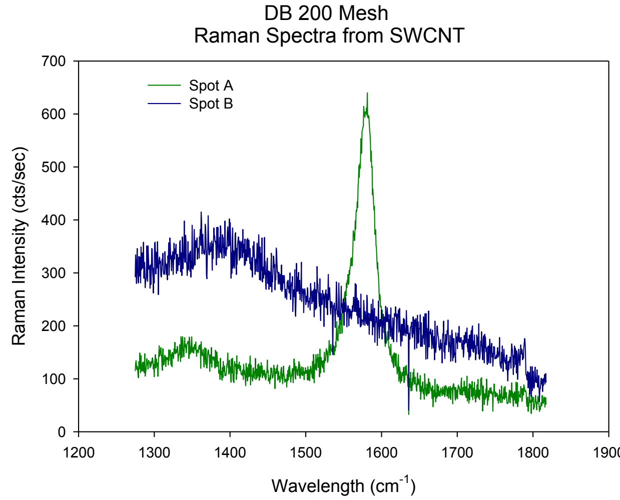


Figure 10. Raman Spectra of two individual spots on an ISDB wire screen that used for the collection of SWCNT sample.

The preliminary tests were performed with a Horiba Jobin Yvon Spex 1250M Research Spectrometer in NIOSH Exposure Assessment laboratories in Morgantown, WV. The results are illustrated in Figures 9 and 10. Figure 9 demonstrates the Raman spectra from a set of SWCNT samples collected on the ELPI stages 2 and 3, respectively. All three feature bands are clearly displayed. Figure 10 shows the spectra from two individual spots located on the surface of an ISDB wire screen. In contrast with Spot A, Spot B is apparently not formed with CNTs

2.1.5 Conclusions

- A practical method for sampling and characterizing airborne CNT particles has been established in this study, utilizing a 13-stage Electrical Low Pressure Impactor in parallel with a 6-stage Integrating Screen Diffusion Battery. The system is capable of monitoring particle concentration and size distribution real-time and collecting size segregated particle samples for detection and quantification of CNT contents in each size fraction by Atomic Force Microscopy. By applying an appropriate deagglomeration pretreatment, the sampled particles can be classified into two categories: tubular (individual nanotubes and/or their agglomerates) and non-tubular (soot, dust, metal catalysts, and other co-existing nano-particles). Physical size and shape characters of tubular particles can also be determined with respect to the diameter, length, aspect ratio and curvatures, respectively. Though a variety of technologies and instruments are available for accurate measurement of overall concentration or size distribution of ultrafine and micron-sized particles, they are not capable of distinguishing engineered CNTs from other particles present in the same airspace. The method developed in this study can identify CNT particles among other engineered and environmental PM and provide well-characterized CNT particle data (such as, structure, agglomeration state, concentration, and size distribution and surface area) that are needed for assessing potential worker exposure to airborne CNTs in an environment involves manufacturing, processing and handling of the raw materials. The technologies developed in this work also provide a foundation for further development of field and personal sampling devices for CNTs.

- The experimental data demonstrated that all types of CNT raw materials examined in this study, including single-walled, double-walled and multi-walled nanotubes, can be dispersed into air to a significant extent with medium powered agitation and very low dispersion air flow. By number counts, the majority particles are in the respirable-size region (< 4 μm) for all types of CNT samples examined; implying that CNTs can possibly become airborne at the workplaces under certain agitation conditions during material manufacturing and handling processes, and expose workers through inhalation and dermal exposure.
- The ELPI measurement data showed that the number-weighted size distribution of CNT particles are widely distributed across all 13 stages of the ELPI including the filter stage ranging from 7 nm to 10 μm. The sizes of CNT particles are varied with the type of CNTs and with the methods by which they were manufactured. The image analysis results by Atomic Force Microscopy showed that CNTs tend to agglomerate rather than to exist as single particles, physically. As deposition efficiency and sites of inhaled particles within the respiratory system largely depends on particle size distribution, the deposition pattern of agglomerated CNT should be similar to those larger equivalent sized non-agglomerated particles. Nevertheless, entrained particles depositing on/in the deep lung surfaces of the bronchioles or alveoli will contact pulmonary surfactants in the surface hypo phase and the agglomerated CNT are likely to be de-agglomerated. Therefore, to correctly determine the extent of exposure to CNTs in the workplace and

assess their potential impact on human health, the measurements of CNTs should include not only their agglomerated form in air but also their de-agglomerated form of post-deposition.

- Experimental data showed that by using a 6-stage ISDB, the number-weighted particle size mode can be resolved in the true nano-region (< 10 nm). Particle in this size can be easily inhaled. It has also been suggested that nanoparticles is capable of rapid translocating directly from human lung into the systemic circulation and cause adverse health effects. (Nemmar et al. 2002**).** By mass concentration, this mode cannot even detectable. However, by number concentration, this size fraction is not neglectable.
- The agglomeration status makes accurate sample quantification and characterization by AFM image analysis difficult. In order to distinguish CNT particles from other coexisting particles, such as metal catalysts and ambient particulate matters, CNT samples need to be deagglomerated prior to the AFM analysis. A deagglomeration method by applying sonication and DMF as a surfactant was used in this study. Further study on development of more effective and quantitative deagglomeration methods is needed.

2.1.6 References

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Xiong, J.Q., Monitoring and characterization of carbon nanotube particles in workplace. Presentation, 2007, ASTM Johnson Conference: Workplace Aerosol Sampling to Meet ISO Size-Selective Criteria, Burlington, VT. July 16-19, 2007

Xiong, J.Q., Heikkinen, M., and Cohen, B.S., Size distribution and characteristics of airborne unrefined carbon nanotube particles., 3rd International Symposium on Nanotechnology, Occupational and Environmental Health, Taipei, Taiwan. Aug. 29 to Sept. 1, 2007

Xiong, J.Q., Heikkinen, M., and Cohen, B.S., Size distribution and characteristics of airborne unrefined carbon nanotube particles., Abstract, AAAR 26th Annual Conference, Reno, NV, Sept. 24-28, 2007.

Xiong, J.Q., Heikkinen, M., and Cohen, B.S., Size distribution and characteristics of airborne particles released from unrefined carbon nanotube materials due to agitation. J. Occup. Environ, Hyg, (to be Submitted).

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