Evaluation of Aerosol Release During the Handling of Unrefined Single Walled Carbon Nanotube Material

Paul A Baron, Andrew D Maynard, and Michael Foley†

National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226
†Comprehensive Health Services, Inc., NASA-JSC

Key Words
Carbon Nanotubes, Aerosol Exposure, Ultrafine Aerosol, HiPCO

SUMMARY

Carbon nanotubes represent a new form of carbon that has several unique properties, including great tensile strength, high conductivity (in some states), high surface area, unique electronic properties, and potentially high molecular adsorption capacity. A number of laboratories are generating small quantities of this material, and commercial interest in the substance is motivating the rapid development of large-scale production facilities. However, little is known of the potential toxicity of the material, or how it should most appropriately be handled to minimize exposure.

In a collaborative effort the National Institute for Occupational Safety and Health (NIOSH), National Aeronautics and Space Administration (NASA), Rice University, and Carbon Nanotechnologies Inc. (CNI) are investigating the nature of the aerosol released when unrefined nanotubes are handled—that is, the material that is aerosolized during the production process, prior to its being purified. Two separate studies have been undertaken on single-walled carbon nanotubes (SWCNT)—a specific form of the material comprised of carbon tubes around 1.5 nanometers (nm) in diameter and up to a millimeter or more in length, and having a single layer of carbon atoms that form the tube wall. Two sources of the material were considered: (1) laser ablation, which leads to a relatively compact powder, and (2) nanotubes formed using the High-Pressure Carbon Monoxide process (HiPCO®), leading to an expanded material that has very low bulk density. Primarily, the propensity for the material to form an aerosol while being agitated was investigated in the laboratory. Aerosol size distribution between 4 nm and 20 µm was measured when the material was agitated in a number of ways. At high agitation levels, a bimodal or trimodal aerosol was formed below 10 µm, depending on the material source, and HiPCO®-generated material led to the release of particles smaller than 10 nm in diameter. However, it was unclear whether these particles represented nanotubes, catalyst particles (used in the manufacturing process), or compact carbonaceous particles. Generation rates were typically two orders of magnitude below those for a similar volume of fumed alumina—chosen because it represents another material that has a very low bulk density and is formed from nanometer-sized primary particles.

The second study investigated dermal and airborne exposures to nanotubes when unrefined material was handled. Material from the laser ablation and HiPCO® processes was removed from production vessels and handled in a clean air enclosure, while aerosol number and mass concentration were continuously monitored. Personal and area filter samples were also taken. Interpretation of the data is somewhat tenuous because instrument response to nanotube particles is not known. However, the results did not indicate appreciable increases in mass concentration when the nanotubes were handled, and number concentration actually decreased during the handling period. When a vacuum cleaner was used to clean up nanotube material, the aerosol concentration increased dramatically, possibly due to inefficient or incorrectly installed backup filters. It was not clear whether the particles detected were nanotube-based or arose from the vacuum motor, although it would seem prudent to exercise caution when cleaning up the material in this way. Large numbers of airborne nanotube clumps were visible to the naked eye, although the visible aerosol and mass concentration readings were not correlated. Analysis of filter samples was confounded by low collection rates, although an estimate of the overall airborne concentration of nanotubes was below 53 µg/m^3. As these samples were dominated by a few large particles on the filters, we speculate that the respirable mass concentration was significantly lower. The levels of nanotube material detected on gloves after the material was handled ranged from 0.2 mg to 6 mg.

Overall, both studies confirmed that at low agitation levels very little nanotube material becomes airborne, and that the individual nanotubes and associated catalyst particles are difficult to separate into isolated particles. However, caution is advised in handling the material until more is known about its toxicity.

INTRODUCTION

Since the discovery of the spherical molecule C_{60} (buckminsterfullerene or *buckyballs*) in the 1980s [Kroto et al. 1985], there has been extensive research into the properties and applications of new forms of carbon. In recent years a specific atomic configuration resulting in long tube-like molecules of carbon (carbon nanotubes) has been intensely investigated; a literature search in one database on "carbon nanotubes" produced a list of over 4,000 articles from the past three years. In their purest form carbon nanotubes are a single layer of carbon atoms in a cylindrical arrangement, resulting in individual carbon molecules around 1.5 nm in diameter, and up to a millimeter or more in length. In this form, the molecules are generally referred to as single-walled carbon nanotubes (SWCNT). Carbon nanotubes may also form as multiple concentric tubes, having diameters significantly greater than SWCNTs: each form has unique properties, and generation of specific nanotube types is a key area of current research.

While commercial mass-production of carbon nanotubes is still at an early stage, the predicted properties of the new products that will use the material are sufficiently attractive to support an intense research and commercialization agenda. Nanotubes exhibit great tensile strength, high conductivity (in some atomic arrangements), high surface area, unique electronic properties, and potentially high molecular adsorption capacity. The range of potential applications that could use these unique properties is currently constrained only by the limited ability of manufacturers to produce large quantities of uniform and well-characterized nanotube material. As a result there is considerable effort at present to refine and scale-up manufacturing processes.

Against this background, very little is known about how likely inhalation and dermal exposure to the material will be during the handling and manufacturing process, or about the toxicity of the material that may be inhaled or come into contact with exposed skin. The extreme aspect ratio of individual nanotubes together with their potentially low solubility in the lungs may lead to toxic mechanisms analogous to those observed with other fibrous particles, e.g., asbestos. Production methods usually lead to the generation of convoluted bundles of nanotubes (nanoropes), generally from 20 to 50 nm in diameter, which in turn form complex clumps with other nanoropes and other material that is present. The health hazard posed by these clumps will depend in part on the ease with which they become airborne, the size of the clumps generated, the propensity for smaller collections of nanoropes to dissociate from the clumps following lung deposition, and the likelihood of individual nanotubes detaching from the ropes in the lung lining fluid. The physical nature of the nanotubes and nanoropes may also lead to some degree of dermal penetration, following deposition on exposed skin, and provide a second exposure route of concern. The potential hazard from dermal and inhalation exposure is further compounded by the presence of small particles of iron or nickel catalyst (typically around 5 nm in diameter) in the unprocessed material from some manufacturing processes. Although these particles are invariably coated in a layer of carbon, little is known of how long they are likely to reside in the lungs, whether the carbon shell is likely to be stripped away within this time, and how the size of the particles will affect their toxicity.

To begin addressing some of these issues, preliminary research has been carried out into the potential for unprocessed SWCNT material to release particles into the air while being handled and to determine the particles' size distribution, which may affect where the fibers deposit in the respiratory system. This report includes the findings from two studies investigating SWCNT aerosol generation under controlled conditions and in the field. In the first instance, unprocessed SWCNT material was agitated, and the concentration and size distribution of the generated aerosol measured. Measurements of particle number, mass concentration, and size distribution were subsequently made at production sites where unprocessed SWCNT material from two types of production processes was being handled.

BACKGROUND

Production processes

One of the principle techniques for nanotube production is to use a transition metal particle as a catalyst in the presence of atomic carbon at high temperature and/or pressure. The two techniques investigated in this report are the laser ablation process and the High Pressure Carbon Monoxide (HiPCO®) process [Bronikowki et al. 2001]. The laser ablation process involves formation of a carbon plug, which contains an intimate mixture of catalyst, and its ablation in an inert gas stream. The resulting product is collected downstream on a coldfinger trap. After ablation of the plug is complete, the plug must be replaced. This approach is inherently a batch process. The collected product is usually fairly compact and the fibers are relatively difficult to separate out; a situation having implications for the release of individual particles into the air.

The HiPCO® process involves introduction of ultrafine iron (Fe) or a combination of Fe and nickel (Ni) metal catalyst particles into a high pressure/high temperature CO gas stream. The product is collected onto a filter and since

it is produced in the gas phase, forms a much expanded mat of fibers. The bulk density of the collected material is on the order of 1 mg/cm^3. Both the laser ablation material and the HiPCO® raw products contain approximately 30% metal catalyst by mass. During secondary processing, the catalyst is removed to the extent possible; however, much of this metal is completely or partially encased in carbon, making complete removal difficult without destroying the nanotubes. Thus, there is a trade-off in catalyst removal versus amount of purified nanotube product.

Potential Health Risk

With the introduction of any new material that has commercial applications, there is concern over material's toxicity and potential routes of exposure. Carbon is generally recognized as having low toxicity in its pure form. However, it is speculated that the small diameter/high curvature of individual fibers may lead to enhanced toxicity through mechanisms, such as reactive oxygen species generation in the lungs. Exposure to compact low-solubility nanometer-sized particles is currently an active area of research [Preining 1998, Oberdörster 2000]. Particle morphology may also interfere with lung clearance mechanisms, which again leads to the possibility of an enhanced toxicity compared to other forms of carbon. Transition metals, on the other hand, are known to have toxic properties, and evidence suggests that the pulmonary toxicity of metals, such as Fe and Ni increases with decreasing particle size.

Using human broncho-pulmonary and human epidermal keratinocytes, it has recently been demonstrated that single wall carbon nanotube exposure demonstrate cellular toxicity. Using Electron Spin Resonance (ESR) spectroscopy, the formation of free radicals, accumulation of peroxidative products and antioxidants depletion in the cells exposed to SWCNT was observed. Additionally, exposure to SWCNT resulted in ultra-structural and morphological changes of cultured human cells. These results indicated that SWCNT exposure may result in accelerated oxidative stress and cause pulmonary and dermal toxicity, as is observed with a number of other chemicals and materials [Shvedova 2001].

Two parts of the human anatomy that are especially susceptible to insult by airborne toxic materials are the respiratory system and the skin. By convention, particles that can enter the respiratory system are broken down into three major regions: (1) dust reaching the gas exchange, or alveolar, region is called respirable dust; (2) dust reaching the tracheobronchial region and alveolar region is called thoracic dust; and (3) dust entering the nose and mouth is called an inhalable dust. Although actual respiratory system deposition is more complex, these three conventions are used for sampling purposes. More detailed, size-dependent, sampling efficiency curves are defined for each of these conventions, but respirable dust is smaller than about 4 μm aerodynamic equivalent diameter (see diameter definitions below), thoracic dust is smaller than about 10 μm, and inhalable dust is smaller than about 100 μm. We investigated airborne particles generated from nanotube production powder to estimate how efficiently small (<10 μm) particles could be generated from those powders. Larger airborne particles can deposit in the upper respiratory system and on the skin. Direct contact with powders can also cause skin deposition. Recent research has indicated that sub-micrometer particles may penetrate through the epidermis following skin exposure [Tinkle 2002].

Aerosol generation requires a force to be applied to powder particles to release small particles into the air. This force has to be applied locally to powder surfaces to separate small particles from the surface by overcoming van der Waals forces, surface tension forces, electrostatic forces or mechanical connections between portions of the powder. Generally, the smaller the particle, the greater the energy required to be transmitted locally to the powder to separate these particles from the surface. Typically, it is difficult to generate a significant mass of particles smaller than about 0.5 μm by mechanical agitation of a powder.

Definition of particle diameters

Particle diameter can be defined in a number of different ways when considering particle behavior in air. Physical diameter often indicates the diameter (maximum extent) observed under a microscope. However, when airborne particle behavior is considered, particle diameter can be defined in a number of different ways. There are several definitions of equivalent diameter, two of which are used in this report:

- *Aerodynamic equivalent diameter (often termed aerodynamic diameter)* of a particle is the diameter of a spherical particle, having a unit density (1000 kg/m^3), that settles under the force of gravity at the same rate as the particle being observed. The settling velocity of unit density spheres can be theoretically predicted to provide an accurate and useful reference definition. Aerodynamic diameter is generally used when particles larger than about 0.5 μm diameter are discussed. It is useful for describing the dynamic motion of particles in the respiratory tract.
- *Mobility equivalent diameter* or *diffusion equivalent* describes smaller particles (<0.5 μm) and is useful as diffusion becomes the dominant mechanism governing particle behavior in the lungs.

Laboratory-based measurements of aerosol particle size within this investigation used mobility diameter for particles smaller than 0.5 μm, and aerodynamic diameter for larger particles, thus most appropriately characterizing particles in relation to inhalation and lung deposition probability. However, field measurements were restricted to measuring

particle diameter using light scattering. The resulting measurement of an optical particle diameter is closely related to physical diameter for spherical particles, but is influenced by particle shape and refractive index. Since the relationships between physical, mobility, aerodynamic, and optical diameters for nanotube clusters are not presently understood, field measurements of particle size distributions and subsequent estimations of mass concentration are only indicative of the aerosol properties of interest. If these particles have significant toxicity, there are further questions regarding the particles' physical form, surface area, cohesiveness, and so forth that must be investigated to select the appropriate metric to use for evaluating workers' exposures.

LABORATORY MEASUREMENTS

Method

The propensity for unprocessed SWCNT material to release fine airborne particles when handled was investigated by agitating a sample of the powder and measuring the size distribution and concentration of the resulting aerosol. Two generation systems were used: A two-component fluidized bed and direct powder agitation. In each case, particle-free (HEPA) filtered air was passed through the generator, and the resulting aerosol was directly sampled by three sizing instruments operated in parallel, to give the size distribution between 4 nm and 20 µm (Fig. 1). The electrical mobility diameter (d_m) of particles smaller than 0.7 µm was sized using two Scanning Mobility Particle Sizers (SMPS). The smallest particles (4.22 nm < d_m < 100 nm) were characterized using a SMPS configured with a Nano Differential Mobility Analyzer (DMA) (TSI Inc., Electrostatic Classifier, Model 3080, using a Nano DMA, Model 3085, and a Condensation Particle Counter (CPC), Model 3022A, St. Paul, MN). Larger particles (69.8 nm < d_m < 777 nm) were characterized by using a SMPS configured with a Long DMA (TSI Inc., DMA Model 3934 and CPC Model 3022A, St. Paul, MN). The largest particles (523 nm < aerodynamic diameter d_{ae} < 20.5 µm) were characterized using an Aerodynamic Particle Sizer (APS) (TSI Inc., Model 3320).

Initial measurements were made using a two-component fluidized bed generator, a device commonly used for generating test aerosols from powders. A small amount of the powder to be generated was mixed with beads (typically around 100 µm diameter). This mixture was placed in a tube and supported by a fine screen. Air was passed upwards through the mixture until the beads were agitated and *fluidized*. As the beads bounced against one another, powder particles were impacted, broken apart, and released into the airflow. The amount of force applied to the powder was dependent on the bead size and the airflow through the bed. When powders contain particles in the size range of interest, i.e., less than 10 µm, this method is an efficient way of generating an aerosol. Unprocessed SWCNT material was mixed with bronze beads, about 70 µm diameter, and the mixture fluidized. We had difficulty forming a good mixture as individual clumps of powder did not readily break apart. When the mixture was fluidized, no aerosol attributable to the SWCNT could be detected above the very low background aerosol associated with the copper beads.

To investigate whether higher agitation energy would lead to the release of measurable quantities of nanotubes, an alternate fluidized bed configuration was devised. Beads and powder were placed in a centrifuge tube, and agitated using a vortex shaker (Vortex Genie, Cole Parmer, Vernon Hills IL). HEPA-filtered air was passed through the tube, and the aerosol characterized using the instrument array shown in Figure 1. Although not quantifiable, this process qualitatively led to significantly more energy being used in the aerosolization process. A measurable aerosol was generated with and without SWCNT material mixed in with the copper beads. Background subtraction of the aerosol associated with the beads alone indicated a measurable component arising from the SWCNT, although we were uncertain as to the magnitude of the bead-related aerosol component following the introduction of SWCNT. Only SWCNT derived from laser ablation was tested using this configuration, and particles between 12 nm and 10 µm were measured using a single SMPS and APS.

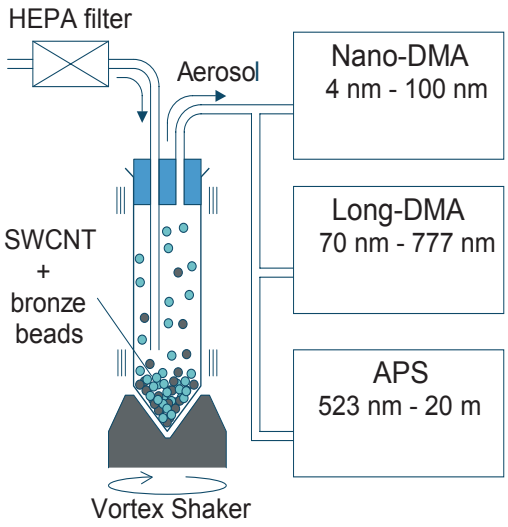


Figure 1. Schematic diagram of the SWCNT generation and characterization system using a vortex shaker to form the fluidized bed.

In an attempt to remove the uncertainty associated with the bead component of the fluidized bed, and to more closely simulate handling of the unprocessed SWCNT material, SWCNT powder was placed in the vortex generator on its own, and aerosol measurements made at various levels of agitation. HiPCO® SWCNT material was used in this generator. Measurements were made of the aerosol size distribution between 4 nm and 20 μm, without agitation, and subsequently, at increasingly higher levels of agitation. At each point three or more replicate measurements of the size distribution were made in series.

Results

Generation of SWCNT aerosol in a conventional fluidized bed did not lead to an aerosol that could be detected above the background associated with the copper beads, and the data is, therefore, not included here.

Generation in the two-component vortex shaker fluidized bed led to a measurable aerosol associated with the SWCNT. Figure 2 shows the resulting aerosol distributions from agitating a small quantity of laser ablation derived SWCNT material over time, after subtracting the background distribution associated with the copper beads. During the generation process nanotube clumps of the order of millimeters in diameter visibly became airborne, although qualitatively the number concentration of these macro-scale particles was low compared to that measured by the instruments. The concentration of SWCNT aerosol below 0.5 μm was seen to decrease rapidly over time, indicating a small component of the nanotube material was readily aerosolized initially. A second experiment using less nanotube material resulted in no detectable particles generated below 100 nm after the initial agitation period. Figure 3 compares the measured size distribution with that from a similar volume of fumed alumina in the same generator (fumed alumina is a low bulk density material with a fluffy appearance, comprised of large agglomerates of primary particles of the order of nanometers in diameter). The comparison indicates generation rates of fine particles from the nanotube material to be approximately two orders of magnitude below that for fumed alumina for similar volumes of material.

Generation of HiPCO® material in the single component vortex shaker fluidized bed led to measurable aerosol concentrations. Figure 4a shows the measured size distribution with no agitation. Particles around 0.1 μm in diameter appear to be released from the SWCNT material, probably as a result of the airflow across the powder. However, concentrations are low and measurement errors are high. Increasing the agitation led to a reduction in particle generation around 0.1 μm, and an increase in the number of nanometer-sized particles released (Fig. 4b), although measurement uncertainty was still too high to allow clear trends to be identified. At the highest level of agitation (Fig. 4c) the measured generation rate was significantly higher than at previous agitation levels, and a clear bimodal distribution emerged. Figure 5 summarizes the results of these measurements, showing changes in the generated aerosol size distribution as agitation increased.

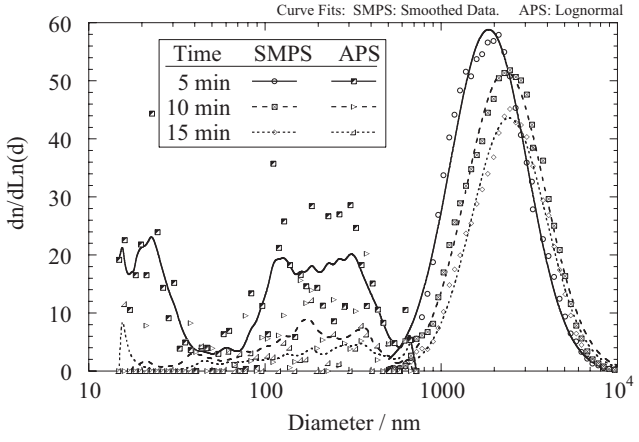


Figure 2. SWCNT aerosol generated using a 2-component vortex-shaker fluidized bed. SWCNT source: laser-ablation process. Background aerosol associated with the beads alone has been subtracted from the distributions. Times refer to the end of each sampling period. Sampling was started 10 seconds after agitation was initiated.

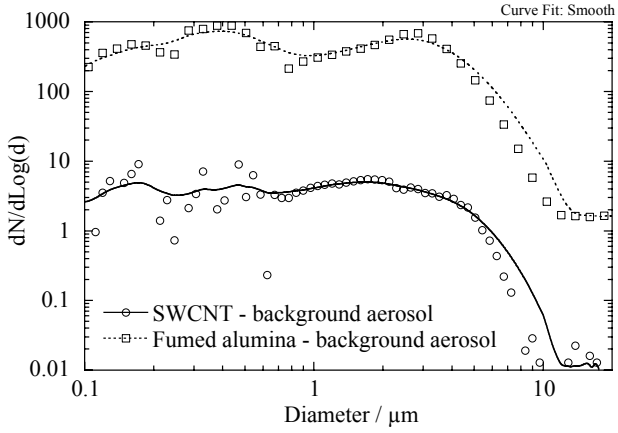


Figure 3. Comparison between the aerosol size distribution generated from similar volumes of SWCNT and fumed alumina when agitated under the same conditions.

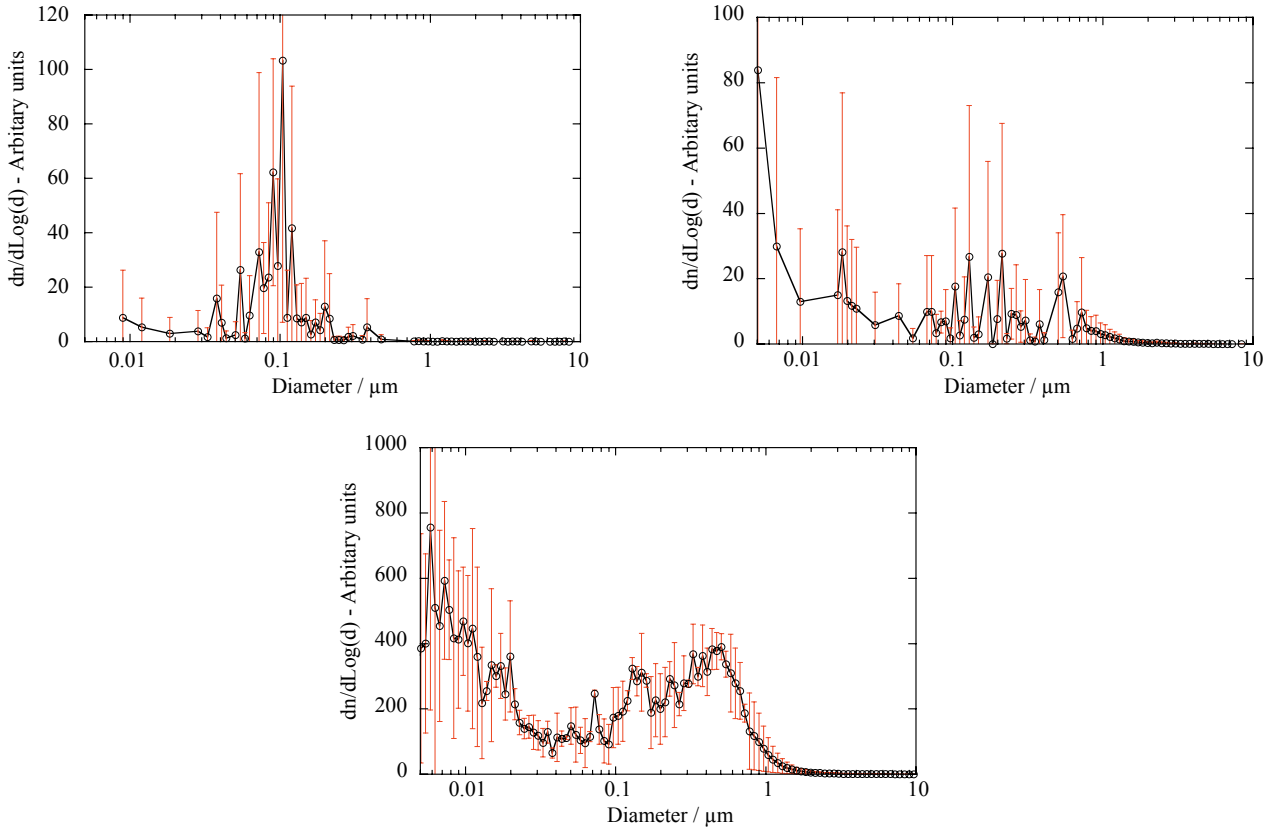


Figure 4. SWCNT aerosol generated using a single component vortex-shaker fluidized bed. SWCNT source: 15 mg material from the HiPCO® process. Each plot is the average of three or more sequential measurements of the size distribution, each measurement lasting approximately 5 minutes. a. No agitation. b. Shaker set to 'shake 2'. c. Shaker set to 'vortex 7'.

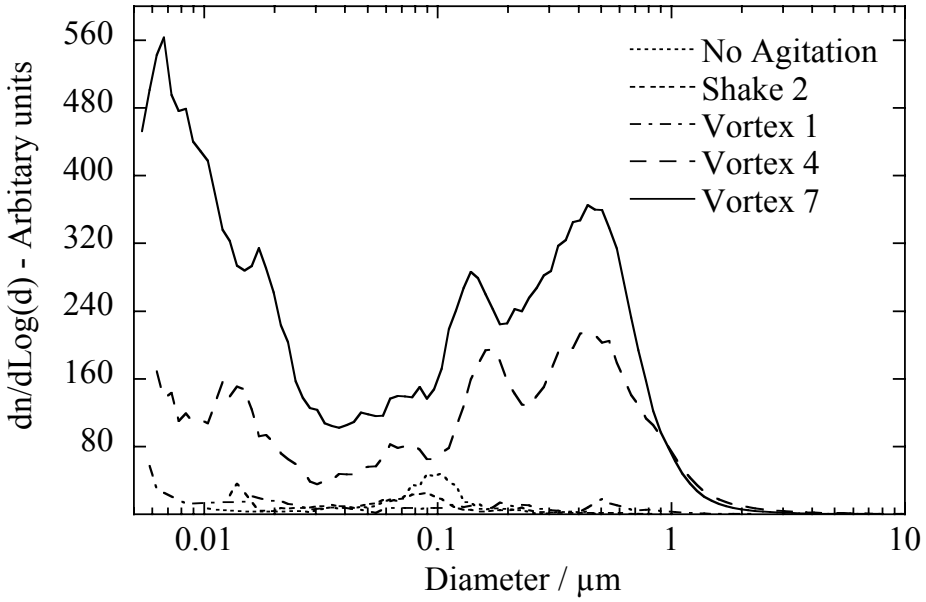


Figure 5. Summary of single component vortex-shaker fluidized bed generation of HiPCO® SWCNT. Data have been smoothed for clarity.

FIELD MEASUREMENTS

Method

Measurements of unprocessed airborne nanotube exposures were made at four facilities where SWCNT material was removed from production vessels and handled prior to processing. It was apparent from the laboratory measurements that bulk nanotube material did not efficiently produce aerosol particles smaller than 10 μm. It was therefore necessary to remove background aerosol from the environment where the nanotube powder was being handled in order to have any hope of seeing the resultant aerosol. An enclosure (approx. 5' x 6' x 7' high) was constructed at each site using 1 1/2" plastic plumbing pipe as a framework and plastic sheet as a covering. The enclosure was sealed, except for a flap, which allowed entrance to the enclosure. Particle-free air was pushed into the enclosure using a high volume sampling blower with a HEPA filter downstream of the blower. This allowed reduction of the aerosol concentration inside the enclosure from several thousand particles/cm^3 to below 50 particles/cm^3 (as measured using a portable Condensation Particle Counter (CPC), model 3007, TSI, Inc. St. Paul MN) in about 30 min. The CPC counts all particles from 10 nm to greater than 1 μm.

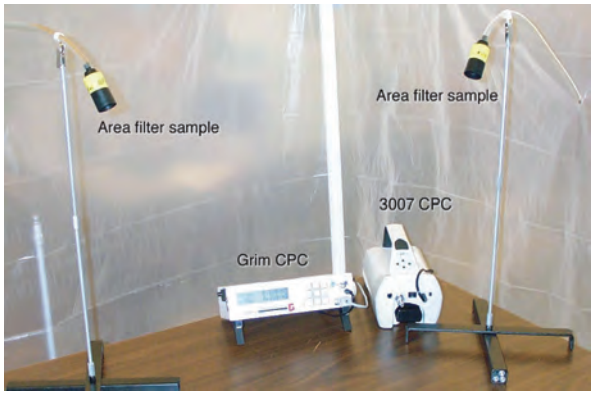


Figure 6. Sampling arrangement for measuring the aerosol generated while handling SWCNT generated using the HiPCO® process at Rice University.

The air inside the enclosure was monitored with several direct-reading instruments, including the 3007 CPC, an Optical Particle Counter (model 229a PC, MetOne, Beaverton OR), and a size discriminating OPC (Portable Dust Monitor series1.100, Grimm, Germany) (Fig. 6). The MetOne OPC gave a total count of particles above 0.3 μm and was used to sense particles in several locations within the enclosure. The 3007 CPC and Grimm OPC were placed in a fixed location near the person who handled the nanotube powder (designated *the worker* in the discussion below).

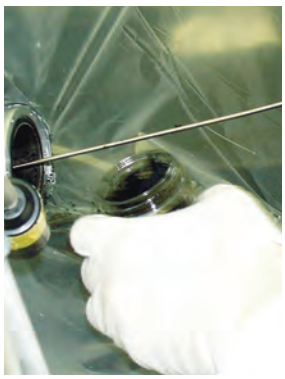


Figure 7. Removal of SWCNT material from the laser ablation facility at NASA JSC.

Filter samples were also taken within the enclosure. A personal sampler was placed on the worker, on a second person inside the enclosure who was monitoring the operation, and at a fixed site near the wall of the enclosure. The personal samples were collected with 25 mm diameter open-faced conductive filter cassettes (used for asbestos monitoring), using methyl cellulose ester filters for metals (primarily iron) analysis [NIOSH 1994]. Because the catalyst appeared to be a fairly constant fraction of the production powder, iron mass analysis was possible as a surrogate for gravimetric measurements. Some of the fixed location cassettes were loaded with 25 mm polycarbonate filters for analysis, using the Scanning Electron Microscope (SEM).

Potential dermal loading was estimated by placing cotton gloves over the rubber gloves normally used by the worker. These were removed immediately after handling the nanotubes and placed in separate sealed plastic bags.

Sampling Locations

Laser ablation facility at NASA. Sampling was carried out during the removal of nanotube material from the experimental laser ablation facility at the National Aeronautics and Space Administration (NASA), Johnson Space Center (JSC) (Fig. 7). A clean-air enclosure was constructed around the entrance to the production vessel and sampling carried out during material removal and cleanup. A vacuum cleaner, fitted with a HEPA filter, was used for cleanup in the enclosure. The filter was later discovered to have been incorrectly fitted, which led to re-suspension of dust when the vacuum cleaner was used.

HiPCO® process removal simulation at Rice University. The production schedule at Rice University did not allow for direct monitoring of material removal from the production facility. Removal was therefore simulated by pouring previously generated material between two buckets normally used for collecting the nanotubes (Fig. 8). Sampling occurred while one bucket was filled with material; while the material was poured between the buckets several times; and afterwards, during cleanup with a shop vacuum cleaner (low-efficiency filter).

Laser ablation process removal simulation at CNI. Sampling was carried out using material produced by laser ablation and the HiPCO® process at Carbon Nanotechnologies Inc. (CNI). Due to space constraints, the collection chamber for the laser process was removed from the production system and placed into the clean air

enclosure for powder removal. Sampling was then carried out while the chamber was opened, the material removed, and the area cleaned. A vacuum cleaner was used during cleanup, but was positioned outside the enclosure with the hose extending into the enclosure.

HiPCO® process at CNI. As in the case of the Laser Ablation material at CNI, the collection chamber from the HiPCO® process was removed from the production system and placed into the clean air enclosure for powder removal. Sampling was carried out during the following tasks: opening the chamber, removing the material, cleaning the area, and dismantling the enclosure. A vacuum cleaner was used for this cleanup, but the vacuum unit was placed outside the enclosure to prevent re-suspension of the dust, and the hose extended into the enclosure.

Results

Direct-reading Instruments

Measurements using the direct-reading instruments provided information on particle number concentration between 10 nm and 1 µm (3007 CPC), particle counts above 0.3 µm (MetOne OPC), particle size distribution above 0.3 µm (Grimm OPC), and an estimate of aerosol mass concentration (Grimm OPC). In the case of the latter, a nominal particle density of 1000 kg/m^3 was assumed. Until a clear measurement of the relationship between optical diameter and mass is derived for nanotube material, these mass data should be treated with caution.

The direct-reading information from the 3007 CPC and the Grimm OPC were combined to estimate the particle concentration as a function of particle size and time throughout the sampling period (Figs. 9 and 10). Particle size distribution is plotted against time, and the concentration is a function of diameter represented by a graduated logarithmic color scale. These plots give a visual indication of changes in aerosol mass and number concentration throughout the nanotube handling processes.

Figure 11 presents a simplified representation of the data, showing summed mass and number concentration as a function of time. The time that key events occurred during each sampling period are given in Table 1.

Filter Samples

Personal sampler filters and gloves were analyzed for iron as a surrogate for total nanotube product mass. All samples were wet-ashed with concentrated nitric and perchloric acids. The filter sample residues were dissolved in 10 ml 4% nitric/1% perchloric acid, while the glove residues were dissolved in 25.0 ml 4% nitric/1% perchloric acid. The sample solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for trace metal content. Bulk material from a previous HiPCO® run was analyzed and contained 30% Fe. While our results may not be representative of other HiPCO® or laser ablation materials, discussions with the producers of these materials indicated that this percentage of catalyst material is probably correct to within about 5% for other materials. Table 2 shows the results of the analysis on personal air samples, while the mass of material on the gloves is given in Table 3.

The filter samples were taken over the time period the worker spent in the enclosure, typically about one half hour.

Figure 8. Pouring HiPCO® nanotube material between containers at Rice University

In some cases (most noticeably when handling the HiPCO® material) large clumps of nanotube material were visible on the filter samples (Fig. 12). In most cases SWCNT contamination of gloves was highly visible at the end of the sampling period (Fig. 13).

Inspection of area samples, analyzed with the Scanning Electron Microscope, showed relatively few particles on the samples (Fig. 14). Samples from HiPCO® SWCNT contained a small number of particles, on the order of 100 µm–1 mm in diameter, having relatively open nanorope structures (Fig. 15). However, most micrometer-sized particles in the analyzed HiPCO® sample appeared to have a compact structure (Fig. 16) with very few nanotubes apparent. In contrast, micrometer-sized particles from the laser ablation process were more clearly comprised of nanoropes (Fig. 17). No evidence of millimeter-sized nanotube material clumps was found in aerosol samples from laser-ablated material.

If we assume that Fe and Ni together constituted 30% of the mass of the nanotubes, the concentration of airborne nanotube material was measured in the range of 0 - 53 µg/m^3. The concentrations during HiPCO® material removal was higher than that during laser ablation material removal. Because of the small number of samples and their similarity to blanks, the confidence level in these results is poor, though it is clear that the concentration of inhalable particles is low.

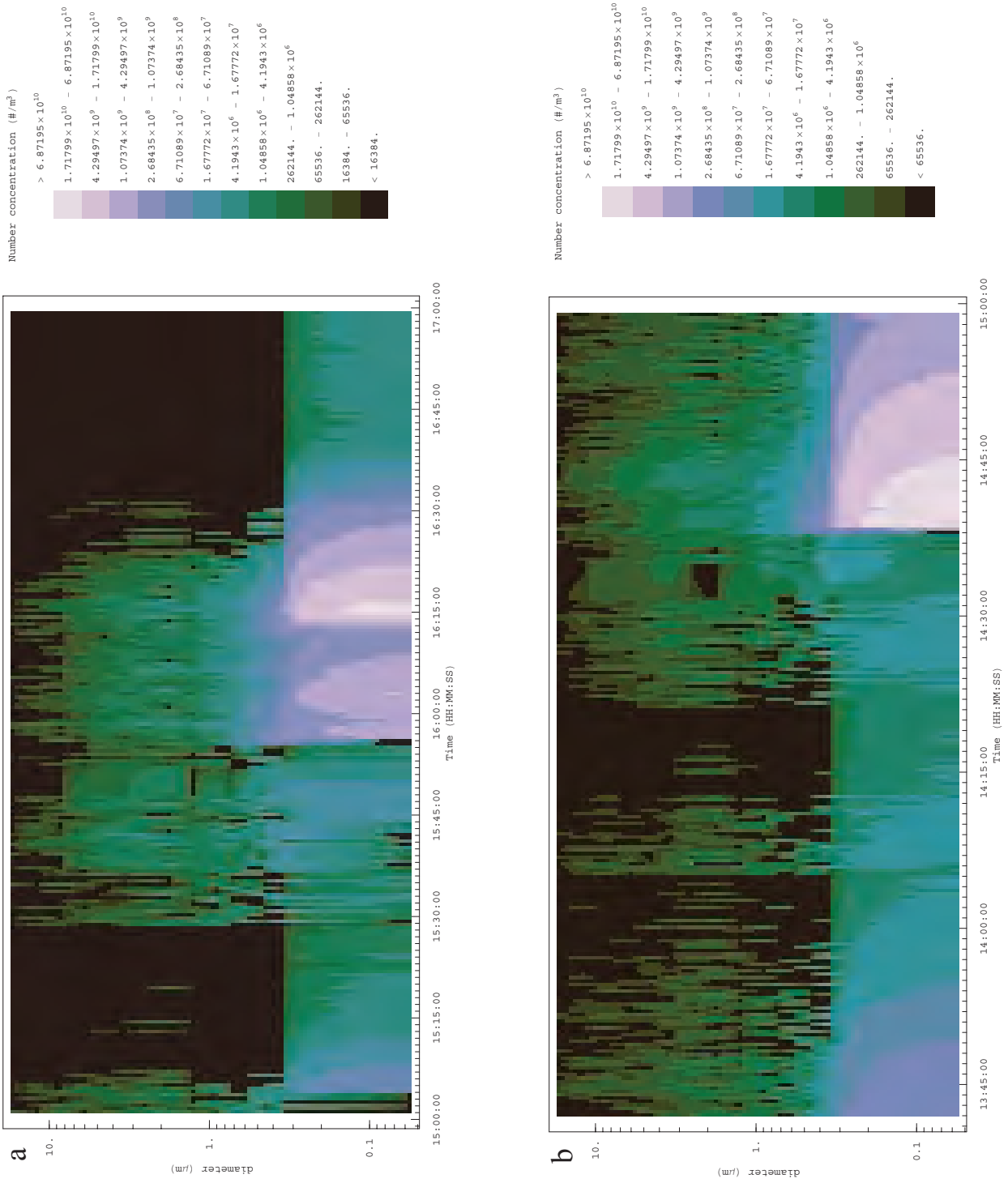


Figure 9. Number-weighted particle size distribution with time for each facility where sampling took place. a. NASA Johnson Space Center . Laser ablation. b. Rice University. HiPCO® material. *Continued on next page.*

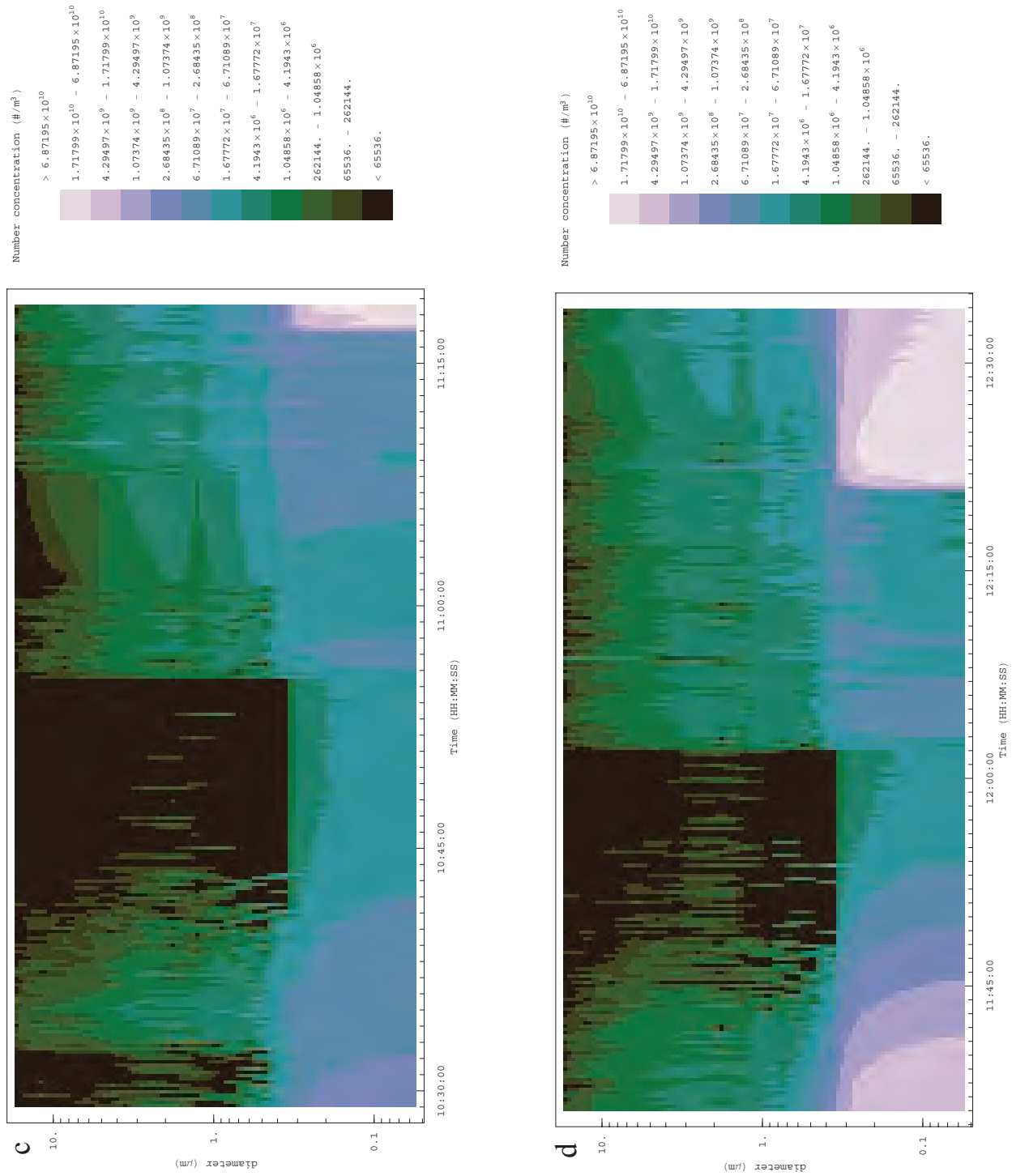


Figure 9 continued. c. CNI. Laser ablation. d. CNI. HiPCO.

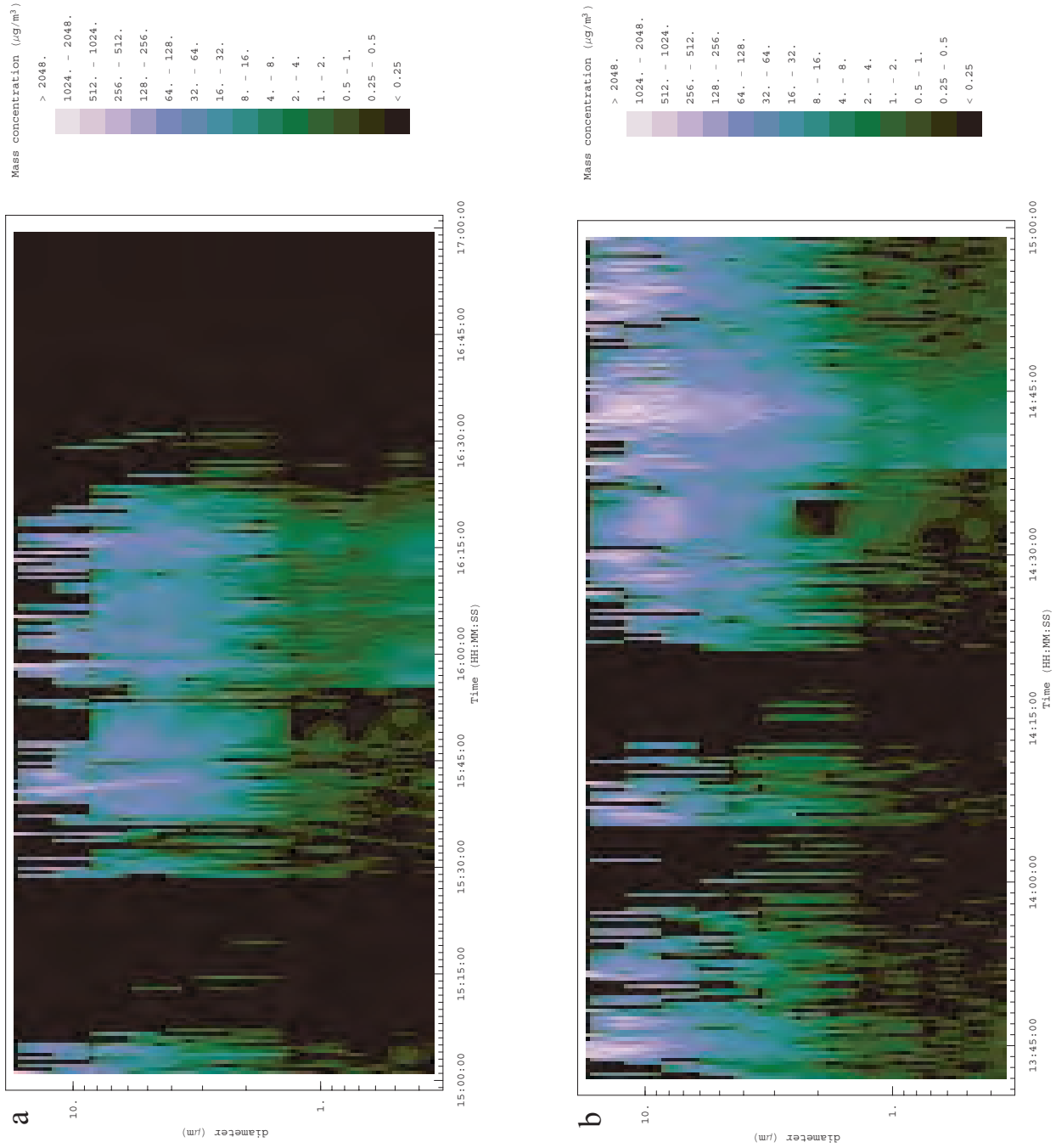


Figure 10. Mass-weighted particle size distribution with time for each facility where sampling took place. a. NASA Johnson Space Center . Laser ablation. b. Rice University. HiPCO® material. *Continued on next page.*

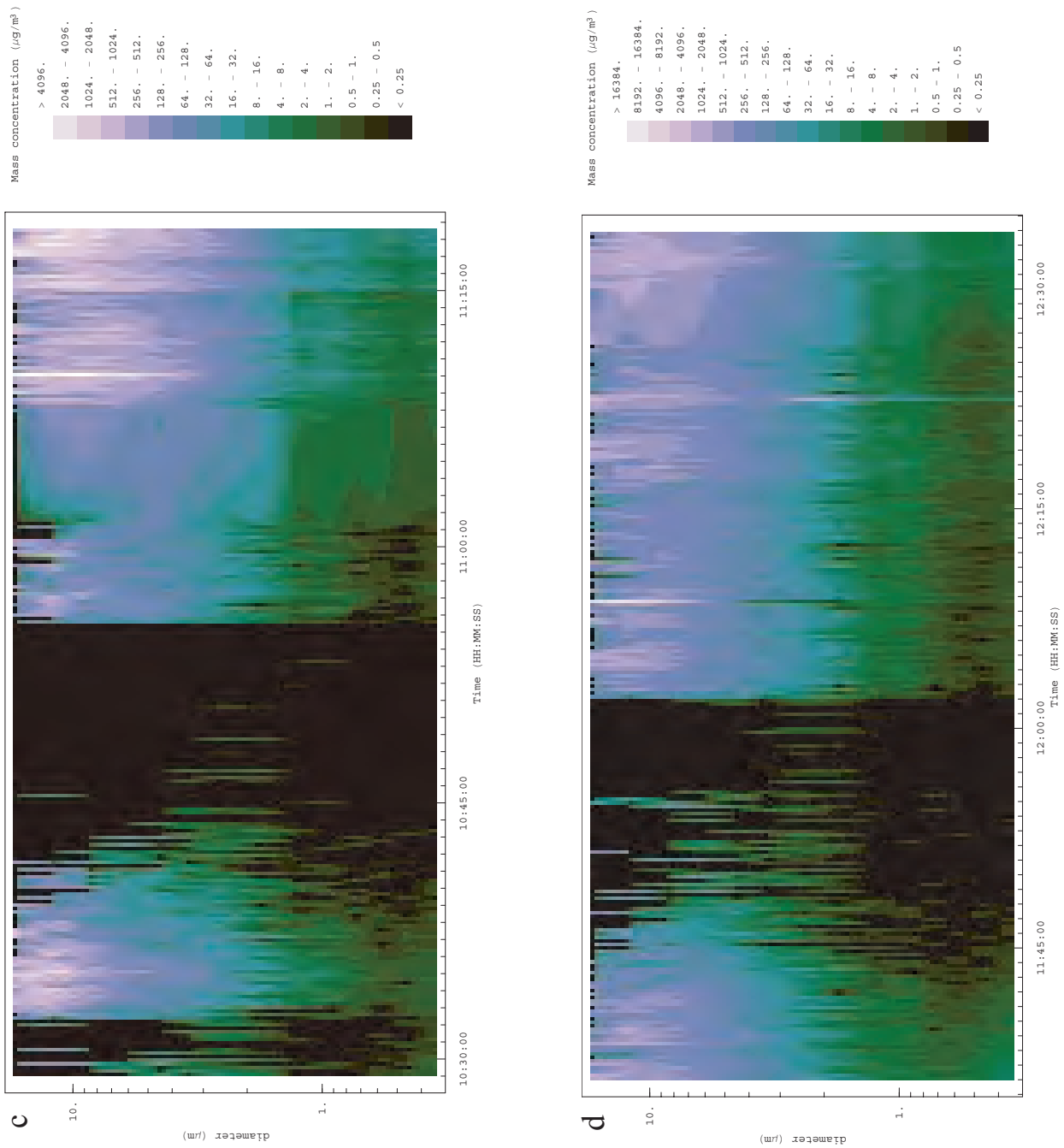


Figure 10 continued. c. CNI. Laser ablation. d. CNI. HiPCO.

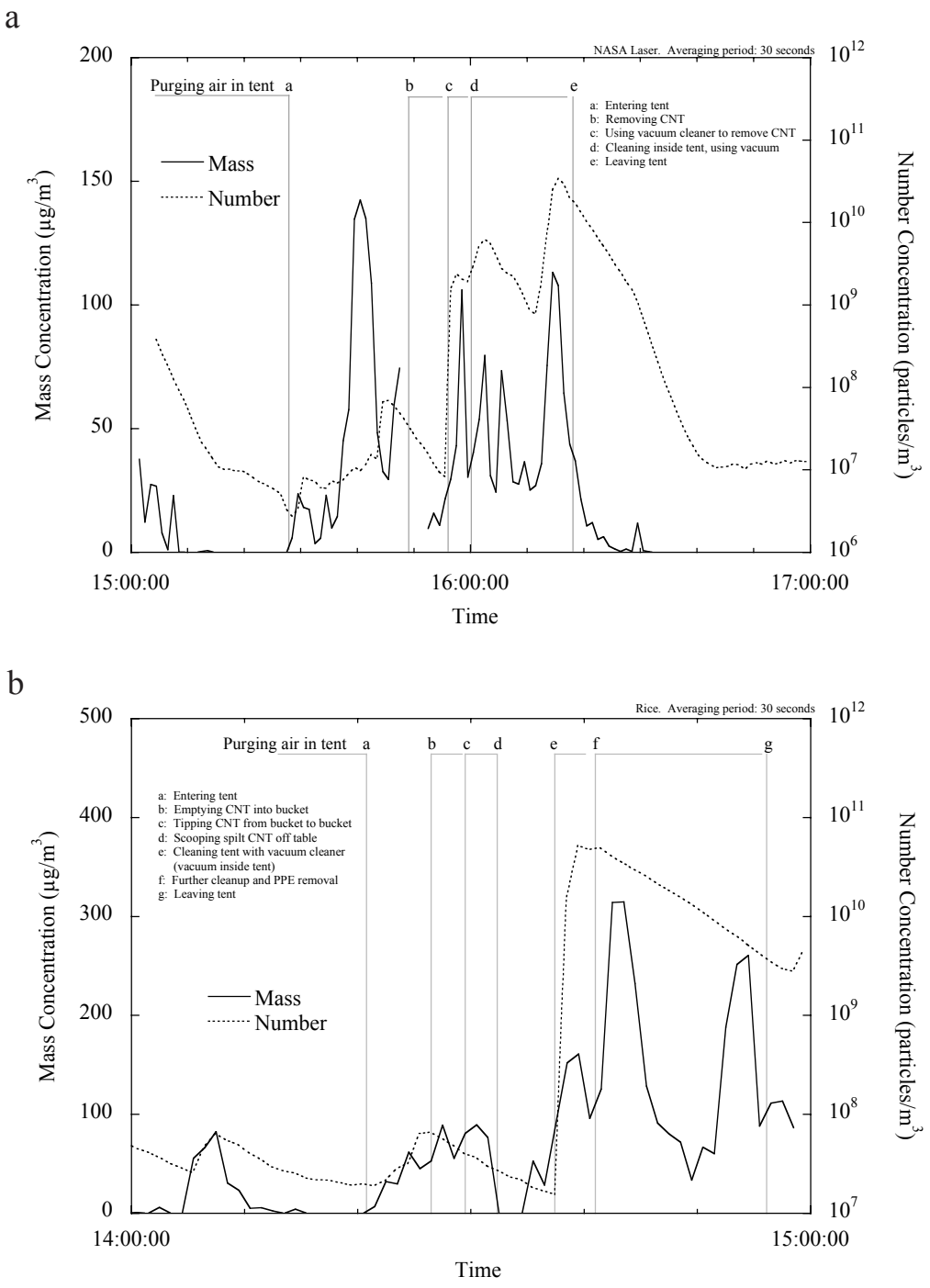
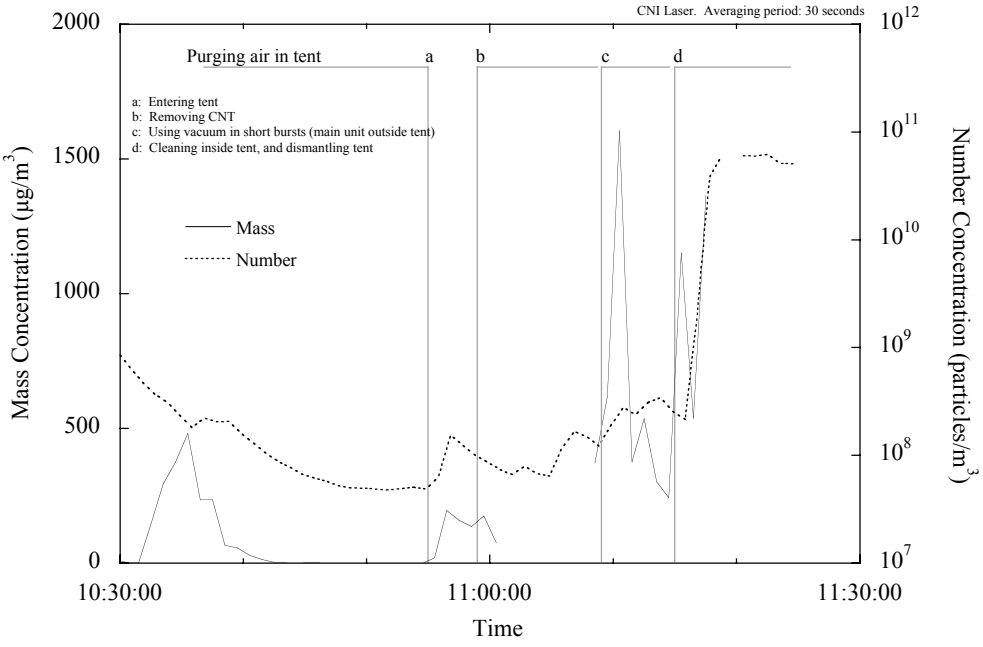


Figure 11. Aerosol mass and number concentration with time for each facility where sampling took place. a. NASA Johnson Space Center . Laser ablation. b. Rice University. HiPCO® material. *Continued on next page.*

c



d

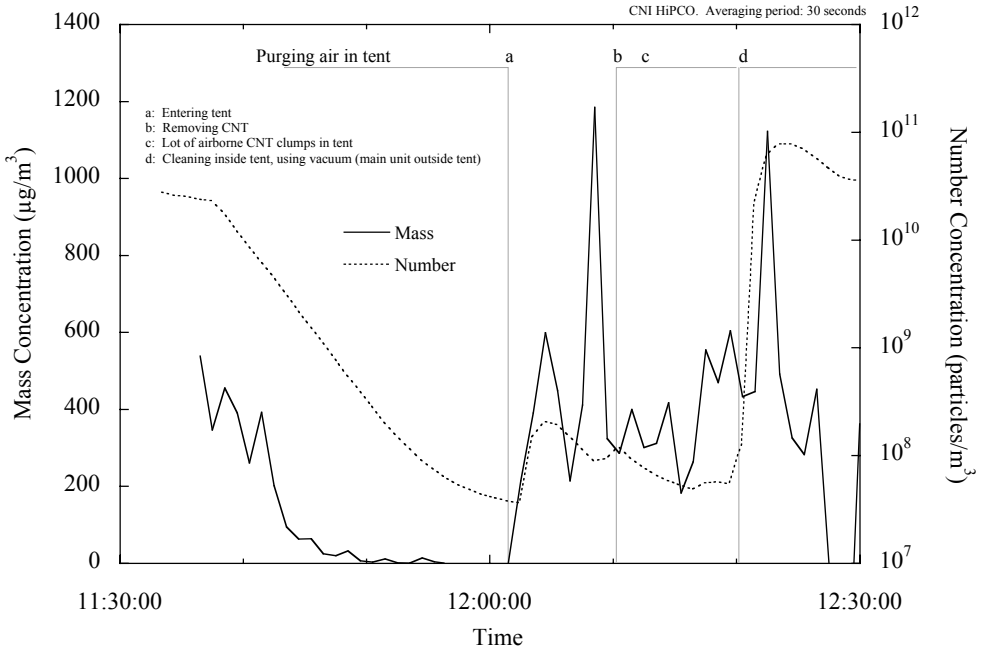


Figure 11 continued. c. CNI. Laser ablation. d. CNI. HiPCO.

Figure 12. Typical personal filter after sampling, showing the presence of large SWCNT clumps.

Figure 13. Photograph showing typical glove contamination with nanotube material at the end of a sampling period.

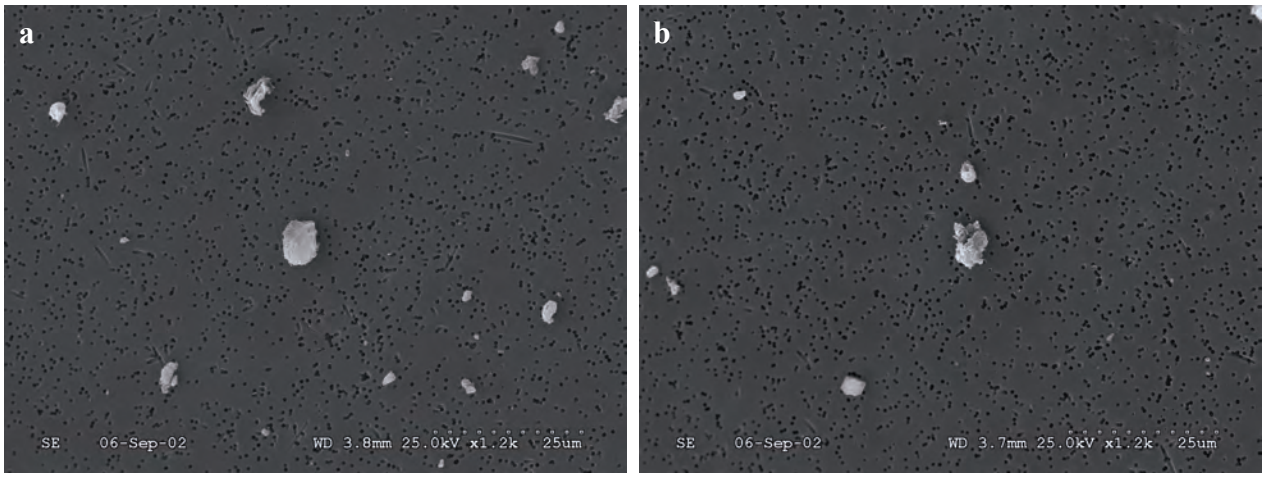


Figure 14. SEM images of area samples from HiPCO® SWCNT aerosol (a) and laser ablation SWCNT aerosol (b)

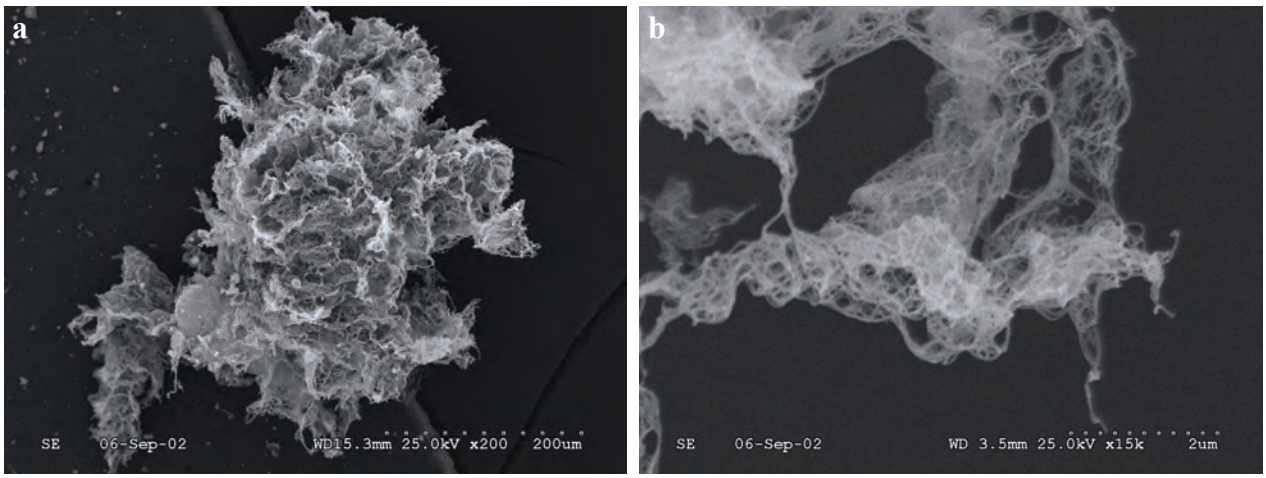


Figure 15. SEM images of a large aerosol particle generated from handling HiPCO® SWCNT.

Table 1. Key events during each nanotube handling operation. Each event is referenced to markers in Fig. 8.

Location	Time	Ref	Event
NASA Laser	15:28	a	Two workers entering tent
	15:48	b	Starting CNT removal
	15:56	c	Intermittent vacuum cleaner use to remove CNT
	16:00	d	Cleaning inside the tent, using vacuum
	16:18	e	Workers leaving tent
Rice HiPCO	14:22	a	Workers entering tent
	14:27	b	Opening CNT container, and emptying into the first bucket
	14:30	c	Tipping CNT from bucket to bucket
	14:33	d	Scooping spilt material off table
	14:38	e	Cleaning inside tent with vacuum cleaner
	14:41	f	Further cleanup inside tent, and personal protective equipment removal
	14:56	g	Workers leaving tent
CNI Laser	10:55	a	Two workers entering tent
	10:59	b	Start removing CNT from container
	11:09	c	Using vacuum cleaner in short bursts
	11:15	d	Cleaning inside tent, and dismantling tent
CNI HiPCO	12:02	a	Workers entering tent
	12:11	b	CNT removal from container
	12:13	c	A lot of large airborne CNT clumps visible to the eye in the tent
	12:19		Large cloud of airborne CNT clumps in the tent
	12:21	d	Cleaning inside the tent, using vacuum cleaner

Table 2. Analysis results of personal air samples from each of the four field sites. Nanotube concentrations have been estimated assuming 30% combined Fe and Ni by mass. Measured amounts below the limit of quantification are shown in square brackets. the metal used to estimate nanotube concentraton is shown in brackets in the fourth column.

Fe: Limit of detection: 0.0643 µg. Limit of quantification: 0.212 µg.

Ni: Limit of detection: 0.0182 µg. Limit of quantification: 0.0601 µg.

Sampling site	Mass Fe (µg)	Mass Ni (µg)	Estimated nanotube concentration from Fe mass (µg/m^3)
Field Blank Average	1.89	[0.03]	
NASA JSC (Laser)	(-0.49)	[0.029]	[0.70] (Ni)
Rice (HiPCO)	0.86	(-0.01)	36.29 (Fe)
CNI (Laser)	(-0.34)	0.284	9.86 (Ni)
CNI (HiPCO)	1.91	0.178	51.73 (Ni)
			52.73 (Fe)

Table 3. Analysis results of glove samples from each of the four field sites (following blank subtraction). Nanotube concentration has been estimated assuming Ni and Fe constitute 30% of the material's mass.

Fe: Limit of detection: 0.161 µg. Limit of quantification: 0.530 µg.

Ni: Limit of detection: 0.0455 µg. Limit of quantification: 0.150µg.

Sampling site	Mass Fe (µg)	Mass Ni (µg)	Estimated nanotube mass (µg)
Blank	388	0.629	
NASA JSC (Laser)	(-267)	65.221	217
Rice (HiPCO) B	1107	4.361	3705
CNI (Laser) B	(-88.5)	258.871	863
CNI (HiPCO) B	1647	158.871	6020

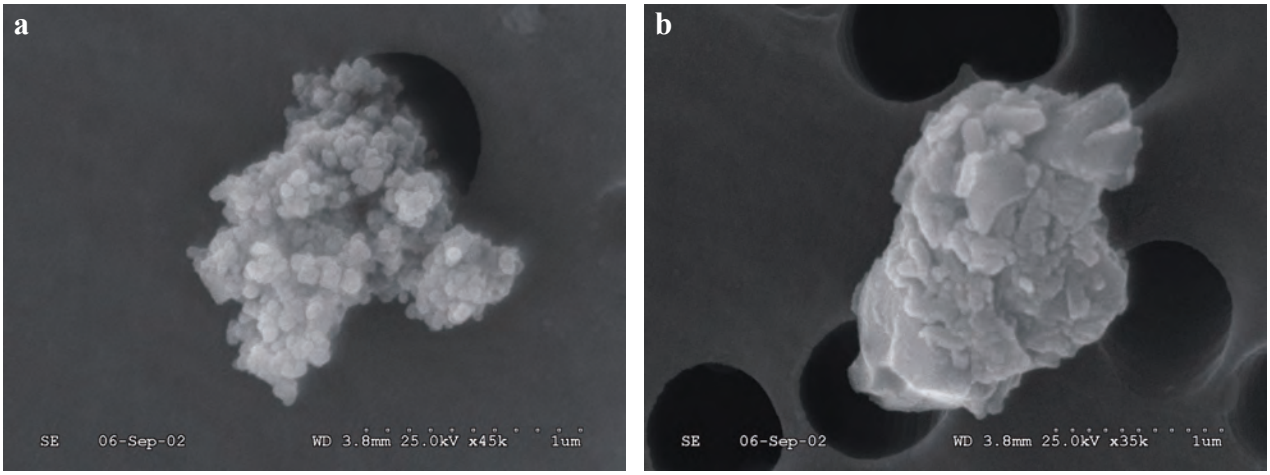


Figure 16. Typical micrometer-sized aerosol particles collected during handling HiPCO® nanotube material.

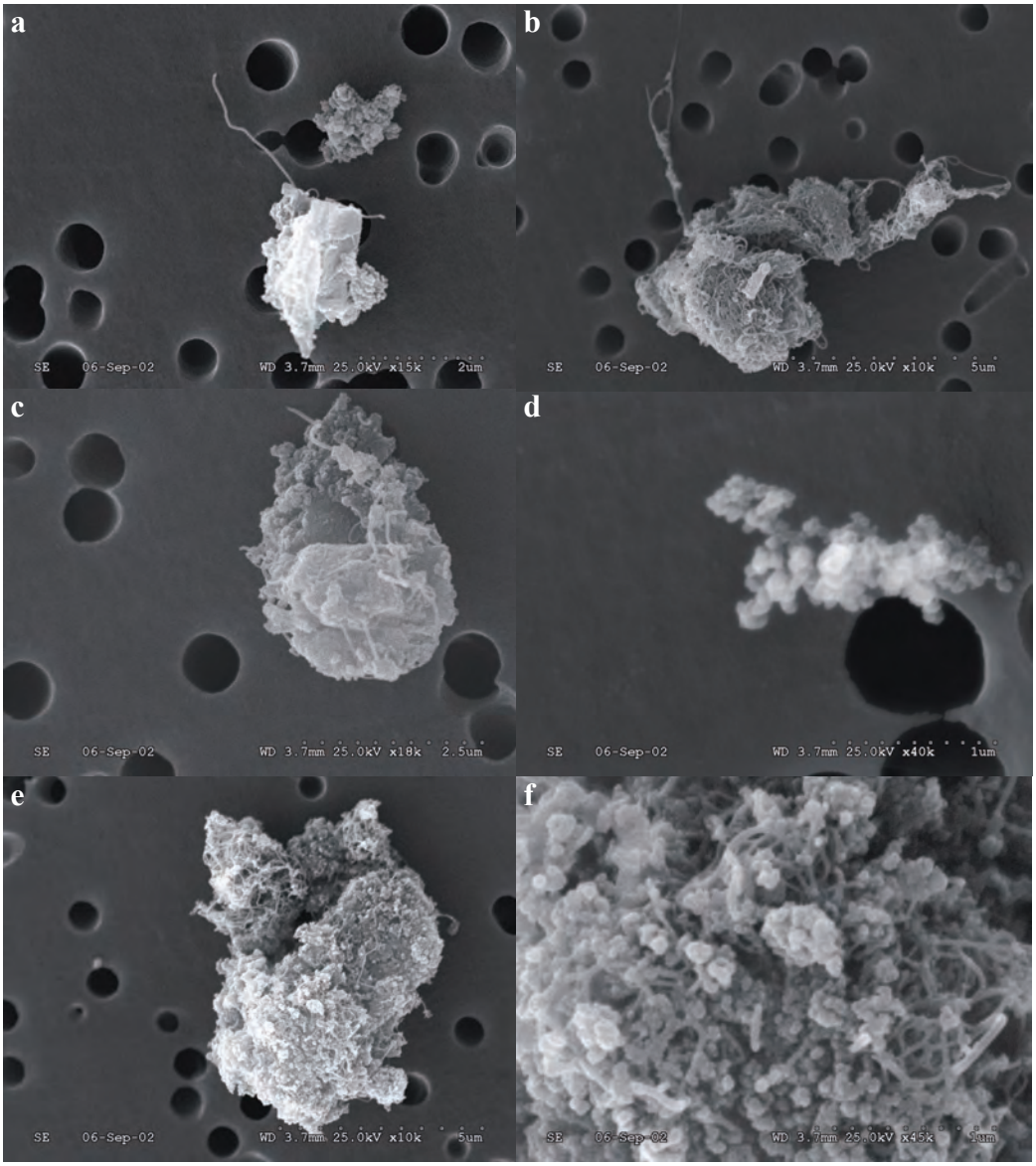


Figure 17. Typical micrometer-sized aerosol particles collected during handling laser ablation nanotube material.

DISCUSSION

The laboratory study indicates that respirable nanotube aerosol generation from production powders is an inefficient process. Relatively gentle agitation in a 2-component fluidized bed did not lead to significant aerosol generation. More energetic agitation initially led to the generation of particles smaller than 100 nm in diameter from laser ablated material, which may have corresponded to small clumps of nanoropes, although the generation within this size range rapidly decreased with time (Fig. 2). Vigorous agitation of the HiPCO® material generated particles below 10 nm (Fig. 3). At this stage it is not clear whether these particles were associated with the nanotubes, compact carbonaceous material in the sample, or catalyst particles. Generation within this size range was stable over 15 minutes, which indicated a steady release of material. Both materials led to particles that had aerodynamic diameters between 1 and 10 μm, which were generated by vigorous agitation, and there was some evidence that the laser ablation material led to particles around 200 nm in diameter being released initially. However, in each case generation rates were around two orders of magnitude lower than those from a similar volume of fumed alumina—another low density material comprised of nanometer-sized primary particles. While there is some debate as to how closely agitation in a fluidized bed will mimic the mechanical handling of SWCNT material, it is reasonable to assume that the results of the lab-based tests are indicative of the generation rates likely to be encountered. Low generation rates from both SWCNT sources were confirmed by the field studies (Figs. 9–11).

The laser ablation powder supplied was compact and difficult to break down into smaller particles on a macro scale (millimeters), so it was expected that smaller particles would also be difficult to release into the air. This assumption appears to be confirmed in the laboratory. The HiPCO® powder was a much expanded material and loosely bound together. Although the powder could readily be broken down into smaller particles in the laboratory, generation of this material was still relatively inefficient. It is quite likely that the expanded nature of the powder prevented transmission of sufficient force locally, within the powder, to overcome the van der Waals forces and release small particles. Examination of variations in aerosol number and mass concentration when nanotube material was handled (Figs. 9–11) appear to support the conclusion that it is difficult to form an appreciable respirable aerosol from the material. In each instance of handling the material in the field, there is no evidence of an increase in particle number or mass concentration during that task. On the contrary, increases in concentration are associated with workers entering the enclosure before the material was handled and aerosol generation during cleanup. In each case, the aerosol number concentration decreased during the nanotube material handling, which indicates no detectable release of very fine material. Mass concentrations between 100 $\mu g/m^3$–500 $\mu g/m^3$ were seen as workers entered the enclosure, resulting from the release of non-nanotube particles from clothing and other surfaces within the enclosure. Similar mass concentrations were seen during cleanup, and were possibly attributable to the same aerosol sources. More significantly, three of the sites showed a large increase in particle number concentration during cleanup, which does not correlate well with changes in mass concentration and indicates the release of very fine particles into the enclosure. In two of these cases a vacuum cleaner was used in the enclosure, and the changes in number concentration correlate closely with its use. This device was clearly a source of sub-micrometer particles both times, although whether these arose from nanotube material being aerosolized during cleanup or particle generation from the unit's motor is unclear. When the vacuum cleaner motor was located outside the enclosure in one instance (Fig. 11c), there was no large increase in number concentration associated with its use, indicating the source of fine particles to be from air passing through the cleaner.

Interpretation of aerosol mass concentration measurements is confounded by uncertainty over instrument response to nanotube particles. The personal air samples placed an upper exposure limit of around 53 $\mu g/m^3$ carbon nanotube aerosol concentration when a worker handled the material. This upper limit agrees reasonably well with the real-time mass concentration measurements in Figure 11. However, the data in Figure 11 have been derived from the assumption of a particle density of 1000 kg/m^3. If the aerosol had been completely comprised of nanotubes, it would be reasonable to use an effective density three orders of magnitude below this, leading to estimated nanotube mass concentrations well below 1 $\mu g/m^3$. However, SEM images of micrometer-sized particles show relatively compact particles, indicating that an effective density between 100 and 1000 kg/m^3 (estimate) may be more appropriate.

Estimates of the nanotube aerosol concentration need to be qualified by visual recognition of large clumps of material released during material handling (Fig. 8). Since our filter samples did not differentiate between inhalable and non-inhalable particles, they will have included some of the clumps (Fig. 12). Based on the effective bulk density estimated above for HiPCO® product, a 3 mm diameter clump would have a mass of 14 μg and an aerodynamic diameter of about 95 μm. Only two or three such particles in a sample would account for the Fe and Ni masses measured. Such a particle would not penetrate to the lungs if inhaled, and, thus, it is highly likely that the respirable fraction of the nanotube aerosol was significantly smaller than the estimated mass concentrations. However, such particles could be readily inhaled and deposited in the mouth or nasopharyngeal region, and, thus, should not be discounted

at this stage as a potential health risk. Exposures to several materials, including Ni, have been associated with increased risk of nasal cancer [Feron et al. 2001].

It may be speculated that the size, morphology, and surface area of inhaled nanotube clumps may be relevant to their toxicity and place a greater emphasis on the number of fine particles generated than on the mass concentration released. In none of the field studies is there any indication that handling the nanotube material leads to an increase in the number concentration of fine particles, suggesting that released particles tend to be larger than 1 μm or so in diameter. These findings concur with the laboratory data indicating that sub-micrometer particles are not readily released at low levels of agitation. The worker at each location was fairly careful to move slowly and attempted to minimize disturbance of the nanotube material during removal from the reaction tube. More energetic processes would be expected to release higher concentrations of nanotube aerosol. There is some question over whether the use of a vacuum cleaner during cleanup led to large releases of small nanotube clusters, or whether the observed particles originated from the device itself. This is clearly an area requiring further investigation, but at this stage it would seem prudent to use HEPA-filtered cleaners with correctly fitted filter units to prevent the potential release of large nanotube number concentrations.

The gloves worn by the worker had as much as 1.6 mg of Fe on them, which indicates as much as 6 mg nanotube product material ended up on the hands (Table 3). Most of this material appeared to end up on the parts of the fingers in direct contact with surfaces, i.e., the inner surfaces of the fingers and palms (Fig. 13). This observation indicates that most of the nanotube material was transferred by direct contact rather than through the airborne route.

Other observations regarding personal exposure to nanotube production material.

The nanotube production processes occurred in airtight systems. However, removal of the product occurred in open laboratories and no effort to control emissions was taken other than handling the material gently. In one laboratory, agglomerates of nanotube material several millimeters in diameter were observed on equipment surfaces prior to our experiments, indicating a release of nanotube material during previous production runs. Additionally, we observed that nanotube material remained airborne for some time, especially the HiPCO® material due to its low density. These two observations suggest that a significant potential exists for extensive contamination of nearby workspace. Workers did, however, wear some personal protective equipment including paper face masks, gloves, and lab coats or Tyvek suits.

NIOSH's primary recommendation for control of toxic materials is to prevent the possibility of exposures by designing processes that prevent the release of the harmful materials. Personal protective equipment to prevent exposures is less desirable, but may be necessary if engineering controls are not feasible.

To reduce their potential exposures, workers can adopt several measures, which do not interfere with the efficient transfer of nanotube material. Because the primary routes of exposure appear to be dermal and inhalation, a glove box arrangement can provide protection for the person handling the nanotubes and prevent an aerosolized release of the material into the rest of the environment. Alternatively, the collection tube for the product can be moved into an enclosed, sturdy structure, similar to that built for this study. However, rather than blowing clean air into the enclosure, the enclosure should be exhausted through a HEPA filter.

If these or similar controls are not feasible, proper personal protective equipment should be used. Skin exposure should be prevented by wearing gloves while handling material. If during handling, SWCNT material becomes airborne around the worker (as when handling large amounts of unrefined material, particularly when removing it from reaction vessels) skin exposure should be prevented by covering all skin surfaces using a disposable suit. The suit should be sealed to the gloves and shoes using tape. The paper masks being used during the SWCNT removal operations in several locations offer poor protection, having protection factors of only about 5. The leakage around the edge of these masks can increase facial skin exposure.

Respiratory Protection

At the current levels of production, the concentrations appear to be low. However, in light of the unknown toxicity of SWCNT production material and the potential for larger scale production, greater protection of workers involved in the nanotube production systems [29–CFR* Parts 1910 and 1926] may be considered necessary. As part of such a protection program, continued monitoring of personal exposures and use of appropriate personal protective equipment is necessary. NIOSH recommends that respiratory protection be used for worker protection only when engineering controls are not technically feasible, such as during the installation or repair of engineering controls, or when an emergency or other temporary situations arise [NIOSH 1987a]. Respirators are the least preferred method of worker protection to air contaminants because of the difficulties generally encountered during implementation of an effective respiratory protection program. Reliable protection depends on the cooperation of the workers to adhere to program guidelines that are critical if respirators are to afford adequate protection.

There are two general classes of respiratory protection: air-purifying respirators, which remove contaminants from the ambient air before it is inhaled; and air-supplied respirators, which deliver an independent source of respirable air (other than the surrounding atmosphere) [NIOSH 1987b]. Both types of respirators can be sub-

* *Code of Federal Regulations*. See CFR in references

classified, based on the type of inlet covering (face-pieces, helmet/shroud, suit, etc.) and the mode of operation. It is essential to fully characterize the hazardous atmosphere where the respirators will be used, including the identity and concentration of the air contaminants.

SUMMARY OF MAIN FINDINGS

- Unrefined SWCNT material released large airborne clumps visible to the naked eye under gentle agitation, but very low numbers of smaller particles.
- Vigorous agitation led to the generation of particles below 10 μm aerodynamic diameter, and the size distribution was dependent on the source of the material and the degree of agitation.
- A few minutes of vigorously agitating material from laser ablation led to very low particle concentrations below 100 nm. It is possible that initial agitation released loosely bound, small, compact clusters of nanotubes from the material.
- Vigorously agitating material from the HiPCO® process led to the generation of particles smaller than 100 nm, which remained consistent over a period of 15 minutes. It was unclear whether these smaller particles consisted predominantly of nanotubes, catalyst particles, or compact carbonaceous particles. The fact that the generation rate was consistent indicates a continual process of particles being broken off from larger clumps.
- Generation rates from all nanotube material tested were approximately two orders of magnitude lower than those from a similar volume of fumed alumina—another low-density material comprised of nanometer-sized primary particles.
- There was no clear evidence of increased aerosol mass concentrations during the handling of unrefined nanotube material in the field. Mass concentrations during handling were generally below those associated with re-suspension of ambient dust due to personal movement, and cleaning operations following handling of material.
- There was no evidence of an increase in particle number concentration during the handling of carbon nanotube material. Rather, in all cases, the field number concentration decreased during the periods when the material was handled.
- Estimated aerosol nanotube concentrations during material handling were below 53 $\mu g/m^3$. However, this value is subject to a number of assumptions and probably represents a significant overestimation of the aerosol's respirable fraction.
- Using a vacuum cleaner to remove spilled nanotube material led to a sharp increase in the aerosol number concentration of between three and four orders of magnitude in three out of four cases. It is possible that a combination of the high suction power and inefficient backing filter led to the device generating large numbers of fine nanotube particles. However it is also possible that the increase in number concentration was associated with the generation of particles from within the cleaner's motor.
- The potential for exposure to unprotected skin was high during material handling. Glove deposits of the unrefined material were estimated to be between 0.2 and 6 mg.

RECOMMENDATIONS

- The low density of unrefined nanotube material leads to large clumps or agglomerates readily becoming airborne during handling. Despite their large size these may be inhalable, and represent much of the potential inhalation mass exposure from airborne material. Visible clumps remain airborne for appreciable lengths of time and are probably the most significant factor in determining nanotube contamination in adjacent work areas, which leads to possible dermal exposure and inhalation of re-suspended material. The authors therefore recommend that material be removed from production vessels within a sealed enclosure, and that material be transported and handled within sealed containers.
- Vigorous agitation of unrefined nanotube material is capable of releasing small quantities of respirable particles into the atmosphere, some in the ultrafine region below 100 nm. While the propensity for the material to form an aerosol while being handled is low when compared to other agglomerated powders having low densities, there is no indication of what may be considered a safe airborne number or mass concentration of nanotube material. The authors therefore recommend that a number of precautions are taken to prevent the unnecessary release of and exposure to respirable particles. Unrefined material should be handled gently to prevent the release of fine particles. Care should be taken during cleanup not to agitate deposited powder vigorously. Appropriate personal protective equipment should be worn at all times when workers come into direct contact with the material (see below). As recommended above, material should be handled within enclosed areas.
- Results indicate that dermal exposure is potentially much greater than inhalation exposure when workers handle SWCNT material. Because preliminary investigations indicate that dermal toxicity may be significant, the authors recommend that all exposed skin be covered during material handling to prevent exposures, contaminated surfaces, and deposition from the air.
- From the results of this study, the authors recommend that personal protective equipment should consist of gloves to prevent skin exposure, as well as respiratory protection, using a full-face respirator that has a high efficiency filter. Where high airborne concentrations of are encountered, such as when removing unrefined material from reaction vessels, the use of a full body suit such as a Tyvek disposable suit to prevent skin exposure is recommended.
- Results from field studies indicate that the use of vacuum cleaners to collect spilled material after handling potentially leads to the generation of fine nanotube particles into the air. While these results are not conclusive, the authors recommend that only devices having correctly installed HEPA filters be used to collect material. An optical particle counter or CPC can be used to monitor the vacuum cleaner exhaust to ensure correct assembly of the filter.
- These results provide an indication of the propensity for unrefined SWCNT material to release respirable and inhalable particles into the air during handling, and an indication of the aerosol particle number and mass concentrations associated with routine handling procedures. The results indicate that under gentle handling negligible increases in number concentration are seen, and mass concentrations are typically less than 100 $\mu g/m^3$. Further research is recommended to distinguish between inhalable and respirable particles released during handling. If the respirable aerosol is found to be highly toxic, it is possible that current routine analysis methods will be inadequate for quantifying exposure. It is, therefore, further recommended that appropriate exposure quantification methods be further investigated.
- Multi-walled carbon nanotubes are stiff, rigid particles with long aspect ratios, that don't form ropes in the same way as SWCNT. Caution is therfore advised regarding extending these findings to multi-walled carbon nanotube material without further research.
- These recommendations are based on the assumption that dermal and inhalation exposure to nanotube material is undesirable. If the material is found to be highly toxic, it is likely that more stringent recommendations on containment and personal protective equipment will be required.

Acknowledgements

The authors would like to acknowledge the support and assistance of Thomas Reese, Lovely Fotedar, Alice Lee and Sivaram Arepalli (NASA JSC); Robert Hauge and Richard Smalley (Rice University); Ken Smith (CNI); Kelsey Seybold Occupational Health Services and the NASA/JSC Occupational Health and Human test Support Office.

REFERENCES

Bronikowski MJ, Willis PA, Colbert DT, Smith KA, Smalley RE [2001]. Gas-phase production of carbon single-walled nanotubes from carbon monoxide via the HiPCO® process: A parametric study. J Vac Sci Technol A-Vac Surf Films *19*(4): 1800-1805.

Feron, VJ, Arts JH, Kuper CF, Slootweg PJ, Woutersen RA [2001]. Health risks associated with inhaled nasal toxicants. Crit Rev Toxicol *31*(3) 313-347.

Kroto WW, Heath JR, O'Brien SC, Curl RF, Smalley RE [1985]. C_{60}: Buckminsterfullerene. Nature *318*:162-163.

NIOSH [1987a]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1987b]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1994]. Elements by ICP: Method 7300. In: NIOSH manual of analytical methods. 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No.94-113.

Oberdörster G [2000]. Toxicology of ultrafine particles: in vivo studies. Phil Trans Roy Soc London Series *A 358*(1775):2719-2740.

CFR Code of Federal regulations [1987]. 29–CFR Part 1910.134: respiratory protection. Washington DC: U.S. Government Printing Office, Office of the Federal Register. Also from: http://www.osha-slc.gov/SLTC/respiratoryprotection/index.html

CFR Code of Federal regulations [1998]. 29–CFR Parts 1910 and 1926: general industry. Washington DC: U.S. Government Printing Office, Office of the Federal Register. Also from: http://www.osha-slc.gov/SLTC/

Preining O [1998]. The physical nature of very, very small particles and its impact on their behavior. J Aerosol Sci *29*: 481-495.

Shvedova A [2001]. Personal communication from A Shvedova to PA Baron. Email. 09/06/2001.

Tinkle SS, Antonini JM, Rich BA, Robert JR, Salmen R, DePree K, Adkins EJ [in press]. Skin as a route of exposure and sensitization in chronic beryllium disease. Environ Health Perspect.