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EXPOSURE ASSESSMENT OF MWCNTS IN THEIR LIFE CYCLE

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Abstract. Multi-walled carbon nanotubes (MWCNTs) are used as a filler in composites to obtain electrical conductivity, and improve mechanical strength and other properties. However, exposure to MWCNTs may pose health risks because of their size, shape, and insolubility. A quantitative exposure assessment method for CNTs is therefore needed. We have developed a promising carbon analysis method that considers the size distribution of elemental carbon. We conducted exposure assessment according to the lifecycle of CNTs. At the first stage, large quantity of CNTs are handled and exposure to neat CNTs is likely to occur. When large quantity of CNTs are handled, enclosure and automated process are strongly recommended. By applying appropriate measures, CNT concentration can be well controlled. Local exhaust ventilation and less-restrictive enclosures were found to work well during the second stage, which involves handling smaller CNT quantities. At measured sites, MWCNT concentrations were below an occupational exposure level proposed by Nakanishi (i.e., 0.030 mg/m³). This analysis method can also be applied to particles containing MWCNTs. At downstream stages of the lifecycle, neat MWCNTs were not observed and concentrations of embedded MWCNTs were lower than 0.015 mg/m³.

1. Introduction

Carbon nanotubes (CNTs) are useful for improving the properties of composite materials, such as electrical conductivity, thermal resistance, and mechanical strength. However, CNTs pose health risks because of their shape, size, crystallinity and low solubility. To date, several occupational exposure limits (OELs) have been proposed by research institutes, for example: 0.03 mg/m³ [1] and 0.001 mg-EC/m³ [2]. These low exposure limits pose several challenges. First, it is difficult to determine such low-level mass concentrations gravimetrically. Second, workplace environments contain particles of nanometer to micrometer size, which are generated from combustion, photochemical reactions, and other means. For this reason, it is not feasible to measure the mass or number concentration of CNTs in isolation from background particles. Third, the recommended exposure limit, 0.001 mg-EC/m³, proposed by the U.S. National Institute for Occupational Safety and Health (NIOSH), is expressed in terms of EC concentration determined by NIOSH Manual of Analytical Methods 5040 [2,3]. This method is sometimes problematic because background carbonaceous particles can show positive effects on the concentration of airborne CNTs. An appropriate analytical method for airborne CNTs requires determining CNTs at the level of 0.001 mg/m³ and distinguishing them from background particles.

EC, the main component of diesel exhaust particles (DEPs), is a surrogate indicator for DEPs. Thermo-optical carbon analysis was developed for assessing the DEP contribution in occupational [4,5] and ambient [6] environments. This method can also monitor airborne CNTs because it measures CNTs as EC, primarily as graphitic carbon. In inhalation exposure studies [7], laboratories [8,9] and workplaces [10–12], EC was used for monitoring airborne CNTs. The key issue in CNT exposure assessments is distinguishing between MWCNTs and ambient particulate matter. Toward this end, we have applied size-segregated sampling and carbon analysis using a modified IMPROVE protocol [13,14] to quantify airborne multi-walled carbon nanotubes (MWCNTs), as shown in **Figure 1**.



MWCNTs easily aggregate/agglomerate into micron-size particles, so micron-size MWCNT aerosols can be determined separately from submicron-size-ECs originating from fuel combustion by taking into account the size distribution of graphitic ECs. This method was applied for exposure assessment in a CNT production facility [15,16].

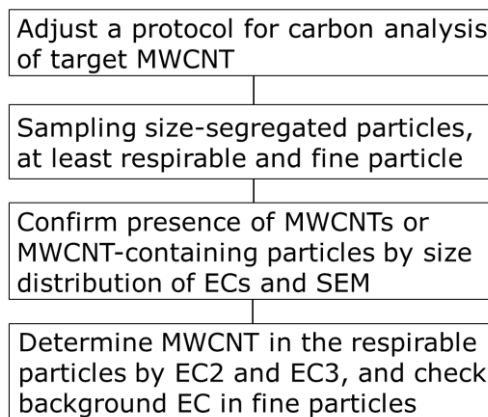


Figure 1. MWCNT exposure assessment procedure of using carbon analysis.

The CNT lifecycle can be categorized into six stages according to the handling quantity and dispersal state of CNTs (**Figure 2**). (1) CNT manufacturing is the first stage. It is conducted in an enclosed furnace without oxygen intrusion. Exposure is considered unlikely during normal furnace operation. After production, however, CNT exposure may occur during maintenance of furnaces and manual handling of CNTs. (2) The next lifecycle stage is manufacturing of interim products, such as masterbatches and CNT-dispersed solutions. The equipment scale and handling quantity are smaller than during production. However, CNT powder is processed manually, and vigorous agitation may release CNTs into the environment. (3) The third stage is manufacturing of products. This stage avoids direct handling of CNTs by using interim CNT-containing products manufactured during the second stage. However, some processes, such as solution drying and paint curing, may release CNTs into the air. (4) The fourth lifecycle stage is the processing of products. Here, physical and/or thermal stress is applied to the composite products, in which CNTs are bound to the base polymer. Release of free CNTs from such composites is expected to be low [17,18]. The fifth and sixth stages are (5) use of products and (6) disposal/recycling.

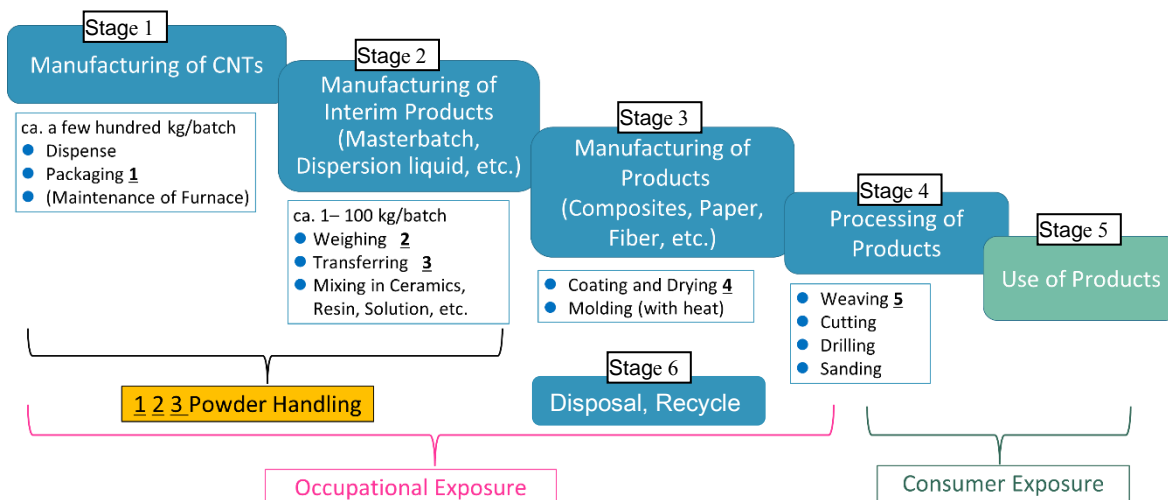


Figure 2. CNT lifecycle.

In this study, we conducted exposure assessments over the course of the first four MWCNT lifecycle stages. This was done by carbon analysis of size-segregated particles to test free CNTs and composite fragments containing MWCNTs. All the facilities were well controlled, and exposure concentrations were below the OEL proposed by Nakanishi [1].

2. Method

2.1. Carbon analysis

In carbon analysis, carbonaceous substances are analyzed by heating samples in an atmosphere-controlled oven. In our research, we applied the method to quantify MWCNTs separately from background particles. First, a filter sample is heated in a helium atmosphere and the evolved substances are detected with a flame ionization detector (FID) are assigned as organic carbon (OC). Then, the atmosphere is changed to oxygen/helium and temperature is raised in steps to three levels (550°C, 700°C, and 920°C). The resulting oxidized carbon, which is reduced and detected as methane by the FID, is assigned as elemental carbon (EC).

There are various types of MWCNTs, which differ in number of graphene layers, impurity content, functionalization, and so on. Temperature and MWCNT oxidation rate reflect the characteristics of individual MWCNTs. Even though MWCNTs have various characteristics, they can be detected as ECs oxidized at 700°C and/or 920°C, designated as EC2 and EC3, respectively. Therefore, the sum of EC2 and EC3 corresponds to the amount of MWCNTs in the sample. EC2 and EC3 are graphitic carbon [18]. MWCNT fibers with greater diameters are oxidized at temperatures higher than 900°C.

In this study, we analyzed MWCNTs in samples collected on a quartz fiber filter with a carbon aerosol monitor (Sunset Laboratory Inc.). We employed a modified IMPROVE protocol (**Table 1**) to characterize and quantify the MWCNTs.

Table 1. Modified IMPROVE protocol.

	Time (sec)	Oven Temperature (°C)	Oven gas
OC1	180	120	He
OC2	180	250	
OC3	300	450	
OC4	300	550	
EC1	360	550	2% O ₂ /He
EC2	600	700	
EC3	360	920*	

*The temperature is 800°C in the original IMPROVE protocol.

2.2. Real-time monitoring

Monitoring was conducted simultaneously at the same points for area sampling. For monitoring number concentrations at workplaces, we used optical particle counter (OPC; KA-80B, RION Co. Ltd.) or optical particle sizer (OPS; TSI 3330, TSI Inc.) for aggregated/agglomerated particles. We monitored number size distribution of 10 to 400 nm with a scanning mobility particle sizer (SMPS; TSI 3910, TSI Inc.).

2.3. Sampling

Area sampling and personal sampling were performed. Area sampling points were set near the source and a few meters away from the source. Since our carbon analysis method requires size distributions for the EC concentration of the sample, a Sioutas cascade impactor (SKC Inc.) was used to collect size-segregated particles with a quartz fiber filter (2500-QAT, Pall). The impactor can classify particles into five fractions by using a flow rate of 9 L/min. The nominal size of each fraction in terms of their aerodynamic particle diameters is as follows: >2500 nm, 2500–1000 nm, 1000–500 nm, 500–250 nm, and backup stage < 250 nm. The experimentally determined D₅₀ of each impaction stage when using a polytetrafluoroethylene substrate was 2,600, 950, 520, and 230 nm [20]. Respirable

particles were collected with a personal sampler (NWPS-2500, Sibata Scientific, Co. Ltd.) operated at a flow rate of 2.5 L/min with the same filter as in sampling with the Sioutas cascade impactor.

2.4 Exposure measurements.

Measurements were conducted at five workplaces over the course of the first to fourth stages of the MWCNT lifecycle (**Figure 2**). At sites 1–3, neat MWCNT powder is handled. At sites 4 and 5, MWCNT-containing materials and solutions are handled. Site 1: MWCNTs are automatically fed from a reservoir into a plastic bag in an enclosed system installed in the facility. Since the enclosed system has a small opening to check operation, small quantities of MWCNTs may leak into the facility. The sampling point is approximately 2 m from the opening and 1-m high. The sampling duration is the same as the packaging process; about 1 h. The background sample was collected at the same point when no operation was underway. Ambient air can enter the facility. The enclosed system is kept at negative pressure and workers wear Tyvek protective clothing with a hood, goggle, gloves, and respiratory protection equipment. Site 2: MWCNT is manually weighed and carefully transferred into a covered mixing machine. The mixture containing MWCNT is then transferred into a plastic bag. The worker and the machine are in a plastic chamber (**Figure 3**). Area sampling was carried out at 2 m from the worker. Local exhaust ventilation (LEV) equipment is installed near the balance and near the opening of the mixing machine. The LEV creates negative pressure inside the chamber. Site 3: A mixture containing MWCNT in the plastic bag are carefully transferred to another equipment for the next process. The opening is set at an upper stage in the facility. An LEV is near the opening of the equipment. Outside air can intrude inside the facility. At sites 2 and 3, workers wear Tyvek protective clothing, gloves, and respiratory protection equipment. Site 4: Polyester fiber soaked with CNT-containing solution is continuously dried and rolled. The location where mechanical stress is applied to the coated fiber is equipped with an LEV. Workers wear Tyvek protective clothing, gloves, and respiratory protection equipment. Site 5: MWCNT-coated yarn is woven. **Figure 4** shows the arrangement of the operator and sampling point. Air sampling “near” is sampling point 2. Personal sampling was conducted by a researcher walking along with the operator.

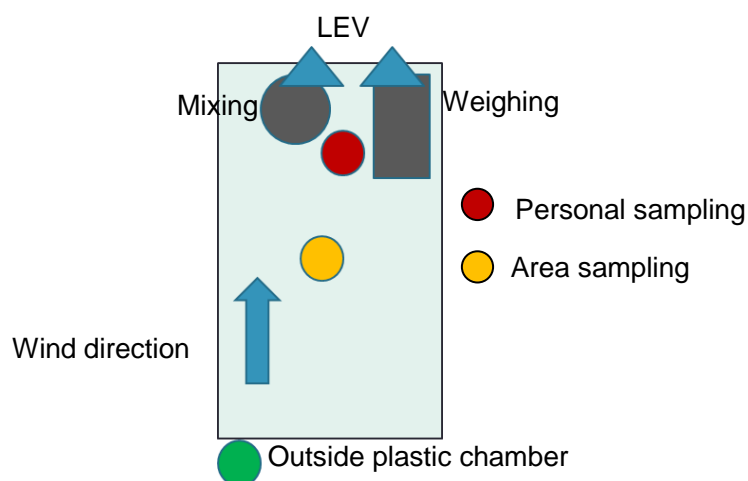


Figure 3. Schematic of sampling site 2 in Figure 2.

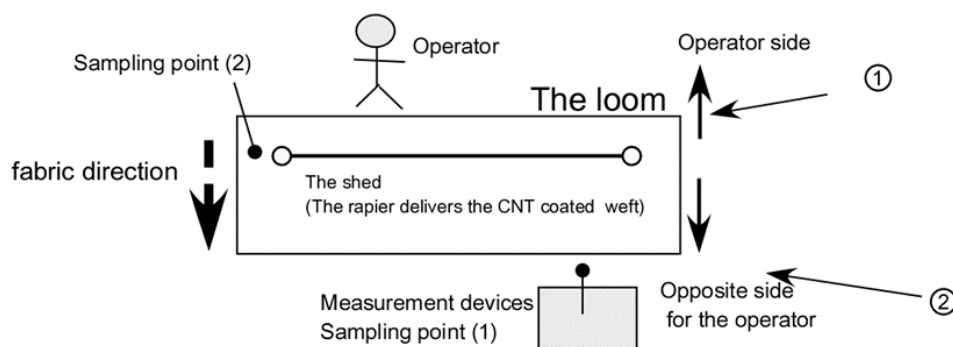


Figure 4. Schematic of sampling site 5 in Figure 2. (Takaya et al. [21])

3. Results

3.1. Handling MWCNT

Table 2 lists MWCNT number concentrations and the corresponding sampling locations. MWCNT number concentrations were detected in the handling large quantities of MWCNTs without an enclosure. When average MWCNT concentrations during a process were less than 0.015 mg/m^3 , direct reading instruments did not detect particle release.

The highest concentrations were observed when the enclosure was not used during handling of large quantities of MWCNTs. In the facility, since packaging is normally performed automatically inside the enclosure, the operator rarely entered the facility and opened the equipment. Exposure concentration was low at 0.020 and 0.010 mg/m^3 by both area and personal sampling, respectively. Clearly, enclosure and automation are effective measures for handling large quantities of CNTs.

At sites 2 and 3, concentrations in the worker's personal breathing zone during handling of smaller quantities of MWCNTs (on the order of 1 kg to 10 kg) were not higher than 0.015 mg/m^3 in our measurements. The concentration on the windward side was less than that observed in personal sampling. According to the results of site 2, we found in weighing tasks, even a loose enclosure had a beneficial effect on exposure conditions. The efficacy of the LEV and the chamber volume affect the concentration inside the chamber. The concentration outside the chamber was low, which shows that the simplified chamber works well to maintain the surrounding environment.

3.2. Handling MWCNT-containing materials and solutions

At sites 4 and 5, we observed no neat MWCNTs by scanning electron microscopy (SEM). MWCNT concentrations shown in **Table 2** are the sum of the MWCNTs, binders, and embedded fibers. Graphitized EC produced from OC cannot be perfectly distinguished from EC produced from MWCNTs; therefore, MWCNT concentrations may be overestimated at these sites. Even though the results include some types of errors, the measured MWCNT concentration is a suitable indicator because an overestimate errors on the side of safety. The cutoff diameter at site 4 is different from that at the other sites because we used a different sampler for respirable particles.

Table 2. MWCNT concentration (mg/m³) and [number concentration] (number/cm³)

CNT Production	Area sampling		Personal sampling		Background Outdoor, or Indoor at night
	Near	Far	Indoor	Outdoor	
Packaging 1	0.020 ^{*1} -0.060 ^{*2} [ND-11000 ^{*3}] by SMPS 10–400nm	0.010 – 0.060 ^{*2}	0.010 – 0.050 ^{*2}	0.002 – 0.010 ^{*2}	0.001 [3000] by SMPS 10–400nm [54]
	[ND-490 ^{*3}] by OPC 300–5000 nm				by OPC 300–5000 nm
Dispersion					
Weighing and Mixing 2	0.005	0.005	0.015	0.002	0.001
Transferring and Molding 3	0.005	0.003	0.005	0.002	0.001
Drying coated solution containing MWCNTs ^{*4} 4	0.015 (near winder)	0.003	0.016	0.002	
Manufacturing of CNT containing Products					
Weaving of MWCNT containing fiber ^{*4} 5	0.005	0.004	0.004		0.001

^{*1} At the opening of the enclosure; ^{*2} Not enclosed, not automated; ^{*3} Background-subtracted; ^{*4} Particulates containing CNTs and fibers were observed, but free CNTs were not observed by SEM observation; MWCNT concentrations in embedded particles.

4. Discussion

We proposed a method for measuring MWCNT exposure and conducted exposure assessments over the MWCNT lifecycle. As shown in **Figure 1**, we categorized the lifecycle into six stages: handling of powdered CNTs (stages 1 and 2) and other stages where exposure to released CNTs might be possible. The main routes of occupational exposure to CNTs are found in stages 1 and 2.

In stage 1, since larger quantities of MWCNTs are handled, strict control measures should be applied to lower worker exposure. Our results show that appropriate protective measures can accomplish this. Airborne MWCNT concentrations in this study were found to be in the range reported previously [12,16]. Airborne MWCNTs seem to be well controlled, at a level of a few to a few tens of micrograms per cubic meter.

Sites 2 and 3 used smaller quantities of MWCNTs. Here, airborne MWCNT concentration was less than a few tens of micrograms per cubic meter, and these concentrations were lower than the OEL proposed by Nakanishi: 0.030 mg/m³. No release into the environment outside the chamber was observed. Smaller-scale handling is often performed in a fume hood, which can also reduce exposure.

Real-time number concentration monitoring can be useful for assessing MWCNT aerosol release. In the present study, outside air intruded into the facility caused sudden increases or fluctuations in the background concentration of particulate matter. In these cases, it is difficult to detect MWCNT aerosol generation by direct reading instruments.

Carbon analysis can be used to measure MWCNTs embedded or bound to organic carbonaceous materials [14] by adjusting the protocol used. In this way, MWCNTs can be distinguished from resins and other base materials in the composite. At least at site 5, SEM analysis indicated no neat MWCNTs, although MWCNT-fiber fragments showed MWCNT extrusion on the fiber surface. Generally, neat MWCNTs are not observed during treatment of MWCNT-containing composite products [21]. Since MWCNTs and the base materials cannot be perfectly separated from each other, base materials contribute positive error to the MWCNT concentration data. Over the course of stages 3 and 4, MWCNT concentration (including the positive error) was lower than the OEL proposed by Nakanishi [1]. In vitro tests have shown that particles containing MWCNTs have a weaker effect than neat MWCNTs [22]. The facilities examined in this study are considered well controlled.

Although carbon analysis method can be applied to exposure measurement of MWCNTs embedded in composite, SEM/TEM observations are essential to confirm if neat MWCNT is released.

5. Conclusion

We performed exposure assessments of MWCNTs at workplaces over their lifecycle by our carbon analysis method, which uses the MWCNT size distribution to distinguish MWCNTs from background carbonaceous substances. In most facilities, MWCNT concentration is well controlled by using appropriate control measures, and workers usually wear protective equipment. Further validation of the method and further examples of its application are needed in order to reach consensus regarding exposure measurements for MWCNTs.

6. Acknowledgment

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The authors declare no conflicts of interest.

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