Approach to the Exposure Assessment of MWCNT by Considering Size Distribution and Oxidation Temperature of Elemental Carbon

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Abstract. Multi-walled carbon nanotubes (MWCNTs) have many beneficial characteristics, but it is concerned that exposure to MWCNTs may pose health risks. As an approach to the quantitative exposure assessment of MWCNTs, we have characterized and determined MWCNTs by elemental carbon (EC) using an aerosol carbon monitor. The EC fractions oxidized at different temperatures correspond sample characteristic such as diameter of MWCNT or origins of particles. As MWCNTs aggregate/agglomerate easily, they are usually observed as micron-size particles. Whereas, EC contained in ambient particulate matter (APM) is mainly observed in fine particles. Therefore, the size of airborne particles is a good parameter to distinguish MWCNT from other carbonaceous particles, especially APM. The size and oxidized temperature of EC suggested the origin of the carbonaceous aerosol samples. Exposure assessment of MWCNT was conducted by utilizing the size distribution of EC in the environment where particulate MWCNT or MWCNT-containing composite was handled. A procedure for exposure assessment of MWCNT-related workplace is proposed.

1. Introduction
Novel carbon nanotubes (CNTs) have many beneficial characteristics, but exposure to them may pose health risks. At present, some OELs (Occupational Exposure Limits) are proposed as follows; 0.0025 mg/m³[1], 0.007 mg/m³[2], 0.05 mg/m³[3], and 0.03 mg/m³ [4]. The OEL proposed by the US NIOSH [2] is derived as elemental carbon (EC) concentration, not mass concentration. Therefore, exposure measurement of CNTs requires a method capable of determining CNTs at least a few to 0.01 mg/m³.

EC is considered as an index of CNT because EC is the main component of CNT. Thermal-optical carbon analysis, which is a sensitive method to measure carbon, has been used to assess diesel exhaust particles (DEPs) in occupational [5,6] and ambient environments [7]. This method has also been applied to monitor CNT concentrations in an inhalation exposure study [8] and to control the
environment of a CNT laboratory [9]. EC has been used as an index of CNT and carbon nanofiber by the US NIOSH [10–12]. However, in an environment where concentration of background carbon is relatively high, the total EC may not represent exposure amount of CNT well. The key issue for exposure assessment of CNTs is the distinction between EC from MWCNT and ambient particulate matter (APM). Therefore, we have applied a modified IMPROVE protocol [13–15] to determine multi-walled carbon nanotube (MWCNT) by carbon analysis. This method can determine MWCNT as graphitic EC separated from other graphitic ECs in APM. As MWCNTs easily aggregate/agglomerate to micron-size particles, by taking into account the size distribution of graphitic ECs, micron-size aerosols of MWCNTs can be determined separately from submicron-size ECs originating from fuel combustion.

Not only for the process in which particulate MWCNT is handled, but also those in which MWCNT-containing composites are used, MWCNTs and/or fragments of those composites can be generated as micron-size particles in the working environment. At present, although the health effects of such fragments are not well known, it is important to collect the exposure data for such particles proactively in the view of an occupational health and life-cycle assessment.

In this paper, we conducted exposure assessment for particulate MWCNT and fragment of MWCNT-containing composite by carbon analysis of size-segregated particles, and propose a procedure to conduct exposure assessments of such particles.

2. Method

2.1. Carbon analysis

There are many variations of MWCNTs having differences of numbers of graphene layers, crystalline structures, and impurity contents. The temperature and rate of oxidation of MWCNTs reflect certain characteristics of individual MWCNT. Therefore, we characterized MWCNTs according to their oxidized temperature. Different types of MWCNTs and other carbonaceous particles were analyzed by a Carbon Aerosol Monitor (Sunset laboratory Inc.)

We employed a modified IMPROVE protocol (table 1) to characterize and determine MWCNT: 1) particles collected on quartz fiber filters were heated under a helium atmosphere to evolve organic carbons (OC); 2) ECs were oxidized at 550°C, 700°C and 920°C under an oxygen/helium atmosphere. The evolved carbon was oxidized to carbon dioxide and then reduced to methane to be monitored using a flame ionized detector. The evolved carbons denoted EC1, EC2 and EC3 are ECs oxidized at different temperatures. EC2 and EC3 are attributed to graphitic carbon [16]. MWCNTs with diameters greater than 150 nm were not oxidized below 900°C.

| 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 |
| EC2 | 600 | 700° or 600° | 2% O2/He |
| EC3 | 360 | 920° |

a. for particulate MWCNT
b. for MWCNT-containing composite, to distinguish MWCNT from base material
c. changed from 800°C in the original IMPROVE protocol
For exposure assessment of fragments of MWCNT-containing composites, we conducted exposure assessment in an environment where MWCNT-containing yarn was woven (see 2.3.2) [17]. The yarn was produced from coating MWCNT with binders on polyester yarn [18,19]. An appropriate protocol was set to distinguish the original polyester, the MWCNT (Baytube C150P) that was coated on the yarn, and the yarn coated with MWCNT. The Baytube was oxidized at 700°C and the polyester yarn and binder were oxidized at 600°C. We applied another modified protocol for this case by setting the temperature of EC2 to 600°C.

2.2. EM observation

For scanning electron microscopic (SEM) observation, aerosol was collected on a polycarbonate filter (pore size 100 nm; Millipore). A field emission SEM (Hitachi S-4700, Tokyo) was used to observe the samples after coating with platinum. Samples for SEM analysis of different types of MWCNTs were prepared by dispersing MWCNTs in 2-propanol with sonication followed by filtration.

MWCNT-coated yarn was observed by transmitting electron microscopy (TEM). A yarn sample cut to ca. 5 mm was embedded in epoxy resin. The embedded resin block was sliced into 0.001 mm-thick sections on a microtome for the optical microscopic observation. Sections in which the MWCNT-coated yarn was detected were sliced into ultra-thin sections of 50–80 nm thick. The ultra-thin sections were examined by TEM (FEI Tecnai G2 sprit, FEI) at an acceleration voltage of 120 kV. The oxidation residue of the carbon analysis, which contains only EC3, was also observed using the same procedure.

2.3. Sampling

We conducted exposure assessments for two different processes: handling particulate MWCNT and applying MWCNT-containing composites. In both processes, the size-segregated aerosol was sampled, and then the aerosol was analyzed using a carbon aerosol monitor. A Sioutas Cascade Impactor (SKC Inc.) was used to collect particles with a quartz fiber filter (2500 QAT, Pall). The impactor can classify particles into five fractions with a flow rate of 9 L/min. The size of each fraction in terms of their aerodynamic particle diameters is: >2500 nm, 2500–1000 nm, 1000–500 nm, 500–250 nm, and back-up stage < 250 nm. Experimentally determined $D_{50}$ of each impaction stage for PTFE substrate are 2600 nm, 950 nm, 520 nm and 230 nm [20].

2.3.1. Handling of particulate MWCNTs. The process monitored was an automated packaging of MWCNT. MWCNT was automatically fed from a reservoir into a plastic bag in an enclosed system installed in a facility. Since the enclosed system had a small opening to check operation, small amounts of MWCNT can leak into the facility. The sampling point was ca. 2 m from the opening. The sampling duration was the same as the packaging process of about one hour. The background sample was collected at the same point when no operation was being conducted (at night).

2.3.2. Handling of MWCNT-containing composite. In the facility where MWCNT-coated yarn was being woven, exposure assessment of fragments of the yarn was conducted [17]. Since there were one loom for MWCNT-coated yarn and over twenty other looms for polyester yarn, fragments of polyester yarn could affect the monitoring of EC. We collected size-segregated samples around the MWCNT-coated yarn loom. Sampling was conducted while the loom for MWCNT-coated yarn was in operation. Background samples were collected at the same point outside the hours of operation (at night) while other polyester looms were operated.

3. Results

3.1. MWCNT oxidation pattern from carbon analysis.
Typical results of carbon analysis and SEM images are shown in figure 1. Thin MWCNTs with diameters less than 10 nm were oxidized as EC2. However, the MWCNTs with diameters exceeding 20 nm were detected mainly as EC3. The temperature at which MWCNTs were oxidized was affected by the diameter of the MWCNT, but not by its length [14] and the size of agglomerate [13]. Although the ratio EC3/EC2 of MWCNTs varies depending on crystallinity, metal content and the amount of sample, EC3 can be used as a good indicator of MWCNTs.

3.2. MWCNT in factories

3.2.1. Packaging process of particulate MWCNTs. We characterized the airborne MWCNT particles by taking into account the oxidation temperature and size distribution of EC2 and EC3. From previous research, MWCNTs, whether simulated or in the real environment, are aerosolized as micron-size particles arising from aggregate/agglomerate [13,14]. When the packaging process was in operation, micron-size EC3 was dominant. At night in the same facility, the amount of EC2 arising primarily from APM was larger than EC3. There were trace amounts of MWCNTs because micron-size EC3 was observed and SEM observation confirmed this result. Most ECs in APM, which is considered as background EC, is characterized as EC2 and dominant in particles collected as fraction smaller than 250 nm. We determine EC3 in all particles collected by SCI as MWCNT by separating from APM.

EC3 concentration was about one tenth of mass concentration. SEM observation showed the presence of small number of single or aggregate/agglomerate MWCNTs.

3.2.2. Weaving process of MWCNT-coated yarn. SEM observation showed the presence of micron-size particles containing MWCNT as fragments of the MWCNT-coated yarn (figure 2). We could not detect single MWCNT fibers in this field survey.

In the workplace, there were a large numbers of polyester fragments from polyester yarn and small numbers of fragments from MWCNT-coated yarn. In order to distinguish between particles with/without MWCNTs, we adjusted the protocol of carbon analysis. The concentration of MWCNTs contained in the micron-size particles did not exceed 0.0053 mg/m³. The respirable mass concentration was about ten times higher than the EC3 concentration.

To confirm that the EC3 was attributed to MWCNTs in the MWCNT-coated yarn, we conducted TEM observations of both MWCNT-coated yarn and the oxidation residue. As shown in figure 3, the polyester disappeared from the yarn after oxidation at 600°C. Therefore, it is thought that MWCNT was detected as EC3.
4. Discussion

A method for measuring exposure to MWCNTs is required to conduct risk management of MWCNTs in the workplace. The analysis of MWCNTs separated from other carbonaceous substances was conducted using a carbon aerosol monitor. MWCNTs were determined by monitoring graphitic carbon. For the carbon monitor measurements, the limit of quantitation was around 0.002 mg. If the sample volume is 1 m$^3$ and the entire area of a single filter is analyzed, the quantitation limit for airborne MWCNT is expected to be 0.002 mg/m$^3$.

Since MWCNTs are oxidized and evolved as EC2 and EC3, EC2 and EC3 are used as quantitative indices of MWCNT.

The size dependency of EC2 and EC3 can be directly applied to an exposure assessment of MWCNTs in the workplace. By analyzing various carbonaceous particles, we presented two-dimensional mapping of size distribution of EC1 (less graphitic carbon), EC2 and EC3 [14]. Generally, MWCNTs are observed as EC2 and EC3 in micron-size particles because they easily aggregate/agglomerate. ECs in APM originating from combustion are observed as EC2 in fine particles. Carbon black (CB) is observed as EC2 and EC3 mainly in micron-size particles. Single-walled carbon nanotubes (SWCNTs) and fullerenes ($C_{60}$) are easily oxidized to evolve as EC1. Interference from these carbonaceous materials should be taken into account.

In addition, this method is applicable for the measurement of MWCNTs in composites by adjusting the protocol to separate MWCNTs from resins or other base materials of the composite.

In figure 4, we propose MWCNT exposure assessment procedure employing this approach. The first step of the procedure is different for particulate MWCNTs and MWCNT-containing composites, because the protocol for the carbon analysis must be changed to correctly measure the target MWCNT. The background concentration of EC2 and EC3 should be measured simultaneously outside the workplace. If outside air does not represent a background of the environment, for example an environment in which no direct intrusion of outside air or other carbonaceous particles are continuously present, the background sample can be sampled in the same place during non-working hours. When the background air contains a high concentration of ECs, assessment of MWCNTs in the workplace should be carefully conducted by analyzing background data.
It is preferable that a person with sufficient knowledge of the processes and of occupational hygiene checks the workplace and decides where and how exposure should be measured. When the gravimetric mass concentration of respirable particles including background is lower than a tentative OEL, for example 0.03 mg/m$^3$ proposed by AIST [4], there may not be needed to conduct carbon analysis. Even if the mass concentration is lower than the OEL, SEM observation of airborne sample or wipe sample is recommended to confirm the effectiveness of the applied control measures.

**Figure 4.** MWCNT exposure assessment procedure by using carbon analysis.

**5. Conclusion**

Exposure measurement of MWCNTs was conducted for the processes of handling particulate MWCNTs and weaving MWCNT-containing yarn by using graphitic carbon as an index of MWCNTs. MWCNTs were observed in micron-size particles as EC oxidized at 700°C and/or 920°C with carbon analysis. Since EC contained in APM is usually observed as EC oxidized at 700°C in fine particles, MWCNTs can be determined separately from background by considering size distribution of ECs. By adjusting the protocol for carbon analysis, MWCNT in MWCNT-containing composite can be analyzed by this approach.

We propose MWCNT exposure assessment procedure employing this approach. The first step of the procedure is different for particulate MWCNT and MWCNT-containing composites, because the protocol for the carbon analysis must be changed to measure correctly the target MWCNT. The background EC should be measured simultaneously. When the background air contains a high concentration of EC, assessment of MWCNTs in the workplace should be carefully conducted by analyzing background data.

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