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Comparison of black carbon concentration and particle mass concentration with elemental carbon concentration for multi-walled carbon nanotube emission assessment purpose

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ABSTRACT

Elemental carbon (EC) can cause lung cancer or inflammation. Therefore, the objective of this study is to identify the possibility of real-time estimation of the EC concentration of multi-walled carbon nanotubes (MWCNTs) for workplace emission assessment. MWCNT aerosol particles were generated at a relatively constant rate over a period of 24 h, and the aerosolized MWCNTs were generally smaller than 1 μm. On-line measurement was performed by using an aethalometer and a scanning mobility particle sizer (SMPS) to determine black carbon (BC) concentration and particle mass concentration of the MWCNTs, respectively. Off-line analysis was conducted according to the National Institute for Occupational Safety and Health (NIOSH) method 5040 to obtain EC concentration of the MWCNTs. Then, correlations among the BC concentration, particle mass concentration, and EC concentration were investigated for the MWCNT particles. The particle number concentration converted from the SMPS measurement data and the BC concentration measured by the aethalometer were found to be in linear relation with the filter-sampling-based EC concentration, when the EC concentration of the MWCNTs was determined by the NIOSH method 5040. It is therefore anticipated that the use of the aethalometer and the SMPS can be of great help to the MWCNT emission assessment.

1. Introduction

Carbon nanotubes (CNTs) have drawn world's attention, since CNTs were first discovered by Iijima [1]. CNTs are categorized into two groups, that is, single-walled carbon nanotubes (SWCNTs, 0.4–2 nm in diameter) and multi-walled carbon nanotubes (MWCNTs, 2–100 nm in diameter), depending on the number of walls comprising the structure [2]. Because CNTs have features of high aspect ratio (length to width ratio > 1000), high electrical and thermal conductivities, excellent flexibility and elasticity, and low mass and density, the CNTs have been employed in many applications. SWCNTs have been used for solar cell, microelectronics such as transistors, and optical instruments such as organic light-emitting diodes [3]. MWCNTs have found application in the fields of aerospace, composite materials, batteries, etc [4,5]. The global CNT market is anticipated to grow continuously from $2.26 billion in 2015 to $5.64 billion in 2020 at a compound annual growth rate of 20.1% [6]. This implies that a lot of workers and researchers handle CNTs in many different kinds of workplaces and laboratories. The CNTs are known to have hazardous effects on human body due to their shape similar to the asbestos [7]. Once the CNTs become airborne, the workers or researchers in CNT-related workplaces or laboratories can potentially be exposed to the danger of inhaling the CNTs.

Lam et al. [8] intratracheally injected SWCNTs, carbon black

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negative control, or a quartz positive control into mice, and then euthanized them over a period of 7 or 90 days. They concluded that the toxicity of SWCNTs was much higher than carbon black and quartz given that the experimental conditions and injection dose were the same. Huczko et al. [9], Warheit et al. [10], and Shvedova et al. [11] also reported the respiratory toxicity of SWCNTs. Not only SWCNTs but also MWCNTs are known to have respiratory toxicity. According to Kostarelos [12], short or tangled MWCNTs could be cleared from the lymphatic system owing to effective phagocytosis by macrophages. However, long and rigid MWCNTs could not be entirely engulfed by macrophages, and consequently, MWCNT accumulation in tissue could cause carcinogenesis. Murphy et al. [13] also reported that long MWCNTs could cause acute neutrophilic inflammation in bronchoalveolar lavage at one week, whereas the short, tangled, and long MWCNTs had a length-dependent pathogenicity similar to that of asbestos. Fenoglio et al. [14] compared cytotoxic activity, uptake, and ability to induce oxidative stress for MWCNTs of two different diameters (9.4 nm vs 70 nm). They confirmed the toxicity of thinner diameter MWCNTs. Poulsen et al. [15] categorized MWCNTs into small and large groups based on diameter and length, and conducted a toxicity experiment on mice. Both small and large groups caused interstitial pneumonia, including perturbation of lipid/cholesterol homeostasis, cell motility, and cell cycle processes. Muller et al. [16] investigated the toxicity of MWCNT agglomerates. Donaldson et al. [17] suggested toxicological paradigms, which could be applied to the respiratory toxicity of either SWNCTs or MWCNTs based on a toxicological database of nanoparticles and fibers.

Dispersion of CNTs can be a critical factor that threatens the health of workers at workplaces. Since a mass-based airborne exposure limit is considered to be the same as the metric used to determine dose-response relationships in animal studies and then derive risk estimates, the mass-based airborne exposure limit is also used in monitoring workplace exposures to CNTs [18]. In addition, elemental carbon (EC) can cause lung cancer or inflammation [19,20]. Therefore, in order to assess the respiratory toxicity of CNTs, it is important to quantitatively monitor the concentration of CNT aerosols, especially in terms related to EC. The National Institute for Occupational Safety and Health (NIOSH) recently suggested a recommended exposure limit (REL): an 8 h time-weighted average respirable mass concentration for CNTs or carbon nanofibers, and set the limit for EC to 1 $\mu g/m^3$ [18]. Thompson et al. [21], Hedmer et al. [22], and Dahm et al. [23] analyzed thermal-optical properties of CNTs from personal breathing zone (PBZ) samples in order to set the REL to 1 $\mu g/m^3$ as the standard for facilities or industrial sites. In terms of CNT morphology, there are various studies that have assessed CNT concentrations using PBZ filter samples and electron microscopy [22–28]. Dement et al. [29] suggested using the transmission electron microscopy (TEM) method in order to improve statistical precision of fiber size determinations for CNTs, improve efficiency, and reduce analysis costs. The NIOSH developed the Nanoparticle Emission Assessment Technique (NEAT) and suggested applying it to assessing field emission of nanomaterials. In particular, the NEAT has suggested using handheld instruments, such as a condensation particle counter (CPC) and an optical particle counter (OPC) for direct measurement, simultaneously with off-line measurement using filter sampling method followed by chemical and microscopic analyses. Some researchers have conducted field studies of CNTs using the suggested NEAT procedures [30–32]. Various studies have also used real-time aerosol monitoring other than CPC or OPC [22,24,33–37]. These studies showed the possibility of real-time detection of MWCNTs for the purpose of exposure or emission assessment in CNT-related workplaces. A variety of studies have been conducted with real-time and off-line methods to assess CNT exposure or CNT emission in workplaces handling nanomaterials. However, it is difficult to distinguish existing nanomaterials with nanomaterial leakage and background concentration. For this reason, most available literature reports only measurement results from nanomaterials emission during the production processes. Moreover, in the view of respiratory toxicity, it is further needed to relate the real-time monitoring with the chemical composition of CNTs.

Carbonaceous aerosols such as CNTs are made up of EC and organic carbon (OC). The EC is caused by incomplete combustion of biomass and fossil fuels, and pyrolysis of biological materials during combustion. The OC is discharged in the form of primary particles or generated as secondary organic aerosols. The EC is optically absorptive, whereas the OC is optically non-absorptive. The NIOSH announced a standard method for determining the EC and OC concentrations of diesel engine exhaust particles collected on a filter medium, that is, NIOSH method 5040 [38]. Ng et al. [39] described the correlations among EC concentration determined by the NIOSH method 5040, black carbon (BC) concentration measured by an aethalometer, and particle number concentration monitored by a real-time aerosol detector such as the scanning mobility particle sizer (SMPS), in respect of diesel engine exhaust emissions. Borak et al. [40] suggested a correlation between EC concentration assessed by the NIOSH method 5040 and BC concentration gauged by an aethalometer, about the diesel particulate matter sampled in a school bus and a workplace for emission assessment. In a laboratory and a manufacturing plant, BC concentration of MWCNTs was reported to change in the range between 7.8 and 321 $\mu g/m^3$ during the handling of MWCNTs [24,34]. This implies that the measurement of BC concentration in addition to particle concentration can be of great help for real-time monitoring of MWCNT emission in workplaces. The relations among EC concentration, BC concentration, and particle concentration were investigated about the diesel particulate matter as reported by Ng et al. [39] and Borak et al. [40] but has not sufficiently been studied in respect of the CNTs.

The global capacity for commercial CNT market in 2013 was estimated to be 2000 tons/year for MWCNTs and 6 tons/year for SWCNTs [41]. Since MWCNTs were estimated to have larger global capacity than SWCNTs, this study aims to focus on MWCNT measurement. The objective of this study is therefore to investigate the relations among EC concentration, BC concentration, and particle concentration in respect of the MWCNTs. The EC concentration of MWCNTs is evaluated based on an off-line measurement method, that is, the NIOSH method 5040. The BC concentration of MWCNTs is measured using an aethalometer. The particle number concentration of MWCNTs is determined by a real-time aerosol detector, that is, SMPS, and then it is converted into the particle mass concentration. In other words, the purpose of this study is to identify the possibility of real-time estimation of the EC concentration of MWCNTs for workplace emission assessment by finding the correlation between the real-time measurements of the BC and particle concentrations of MWCNTs and the off-line measurement of the EC concentration of MWCNTs.

2. Experimental method

2.1. Aerosolization of MWCNTs

Fig. 1 shows the schematic of experimental setup. MWCNTs (Model CM-95, Hanwha Chemical, Republic of Korea) were dispersed in deionized water and aerosolized using an electrostatic assisted axial atomizer (EAAA) developed by Lee et al. [42]. According to specifications provided by the manufacturer, the bulk density of the MWCNTs used in this study was 0.1 g/cm^3. In order to