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Validation of the Analytical Method for Different Types of Carbon Nanotubes and Carbon Nanofiber and Exposure Assessment of Workplaces

탄소나노튜브 및 탄소나노섬유의 분석방법 설정과 이를 이용한 국내 취급 사업장 노출평가

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ABSTRACT

Validation of the Analytical Method for Different Types of Carbon Nanotubes and Carbon Nanofiber and Exposure Assessment of Workplaces using Analytical Method

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Objective The major purposes of this study were to establish analytical method of elemental carbon (EC) in carbon nanotubes (CNTs) and carbon nanofiber (CNF) and to assess the airborne CNT at the workplaces Specific aims of this study were 1) to set up the analytical methods of EC according to the types of CNTs and CNF, 2) to evaluate the correlation between EC and the metrics measured by real-time monitors, and 3) to measure the CNT at the workplaces in Korea using EC sampling and real

time monitors.

Methods The study was consisted of three parts; First, to evaluate existing methods and proposing new method for EC in CNT and CNF using bulk CNTs/CNFs, second, to evaluate airborne CNTs in exposure chambers. Third, to evaluate airborne CNTs at the workplace. Domestic CNTs/CNFs were used to evaluate the EC analytical method and airborne CNT in the exposure chamber.

Based on guidelines of National Institute for Occupation and Safety (NIOSH) for air sampling and analytical method development and evaluation, recovery rate experiment for EC in CNT and CNF were performed to establish analytical methods. The existing methods such as NIOSH Method (NIOSH Manual of Analytical Method) 5040, Modified NIOSH Method 5040 and Modified IMPROVE (Interagency Monitoring of PROtected Visual Environments) A method were tested and a new method to increase recovery rate with better precision was also proposed. Both filter-based sampling for EC and real-time monitoring for aerosol monitoring was performed in exposure chambers equipped with HEPA filter to evaluate the correlation between EC measurements and real time nanoparticle sampling devices. Exposure assessment of workplaces was targeted to one manufacturer and one laboratory.

Results For single-walled carbon nanotubes (SWCNTs) and CNF, NIOSH Method 5040 proved to be appropriate with the high recovery rate (97.7±5.4%) and good precision (pooled relative standard deviation; 0.0012). For multi-walled carbon nano tubes (MWCNTs), existing analytical methods such as NIOSH Method 5040, Modified NIOSH Method 5040 showed a wide range of recovery rates by MWCNT types with relatively large standard deviation. The new proposed method which

increased temperature to 930 ℃ and time to twofold of the thermal carbon analyzer showed a good recovery rate of 99.4±5.2% and a high precision with pooled relative standard deviation of 0.0028.

In the exposure chamber, a relatively good correlation was found between EC level and Black carbon (BC) measured by Aethalometer (the Pearson correlation coefficient was 0.73) and surface area concentration by SAM (the Pearson correlation coefficient was 0.16) though the former was an integrated sampling and the latter was a real time monitoring instrument. At the workplace, airborne EC concentration was 6.03+1.70 $\mu g/m^3$ in A workplace and 2.70+0.88 $\mu g/m^3$ in B laboratory. Twenty-eight samples among thirty-four samples (82%) of the total EC samples exceeded the recommended exposure limit (REL) of one $\mu g/m^3$ suggested by NIOSH.

Conclusion NIOSH Method 5040 was proven to be appropriate to analyze SWCNT/ CNF. A new method was proposed for MWCNT. EC for CNT integrated sampling and Aethalometer for real time monitoring may be the useful to CNT exposure assessment (the Pearson coefficient was 0.79). However, other nanoparticle sampling devices and electron microscopy analysis in parallel would be necessary to understand to CNT exposure assessment. During the monitoring of workplaces, most of EC samples exceed the REL of NIOSH. Exposure control strategy and hierarchy of controls is recommended to mitigate exposure to CNTs.

Keywords: Carbon nanotube, Carbon nanofiber, NIOSH Method 5040, Elemental carbon, Exposure assessment

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1. Introduction

Nanotechnology is an emerging area of technology development that involves science and engineering of matter at the nanoscale of approximately 1-100 nanometers [ASTM, 2006]. CNTs and CNFs are some of the most promising materials as a result from nanotechnology. Introduction of these nanomaterials and applied products using them in the market has increased greatly in the last decade [Thostenson et al., 2001; Invernizzi 2011]. The applied products and their application CNTs and CNFs are used in various industrial fields including biomedical applications, electron field emitters, conductive plastics, semiconductor devices, chemical sensors and catalysts, and medical devices [Endo et al., 2008; Wang et al., 2011, McKinney et al., 2009, Chakravarty et al., 2008, Endo et al., 2008]. The global production for CNTs has increased from 30 tons in 2008 to nearly 3,400 tons in 2010 [Innovative Research and Products Inc., 2011]. With the expansion of this market, the possibility of worker exposure from handling these nanomaterials is expected to increase [Dahm et al., 2012].

There is little information on the toxicological data and adverse health effects of CNT/CNF. It has been known to cause pulmonary effects such as inflammation, granulomas, and pulmonary fibrosis in animals tested in previous studies [NIOSH, 2013].

There is no standard analytical method to evaluate the CNTs/CNFs. NMAM (NIOSH Manual of Analytical Method) 5040 has been widely used to evaluate the CNT/CNF from elemental carbon (EC) analysis [NIOSH, 1994; Birch, 2004a, b], but it has been effective to evaluate diesel particulate matter as element carbon. Although some modified methods for EC analysis such as the IMPROVE A, the

NIOSH, EUSAAR_2 (European Supersites for Atomospheric Aerosol Research, www.eusaar.net), and quartz protocols have been suggested [Chow et al., 1993, Birch and Cary, 1996, Cavalli et al., 2010]. Several studies proposed the modified exist method [Myojo et al., 2009, Ono-ogasawara et al., 2011]. However, none of the studies evaluated of the reliability.

A number of CNT exposure assessment studies in Korea have found CNT exposure mass concentrations within the range of 0.1 to 12 μg /m^3 among area sampling [Lee et al., 2010, Ji et al., 2013]. Several studies confirmed that CNT exposure formed agglomerates using electron microscopy analysis [Ji et al., 2014a, Ji et al., 2014b]. However few studies have been analyzed using the NIOSH Method 5040 for determining CNT exposure.

Accordingly, this study uses several real-time monitor to provide various metrics for particles whereas filter-based sampling is used to monitor the EC mass concentration of particles in the air. However, some real-time monitors (e.g. SMPS, OPC) are commonly used to determine particle of spheres and are not applicable for elongated particles. Therefore, these monitors could underestimate evaluation of CNTs due to their non-spherical form and the estimated values of CNT density and particle diameters. Recently, several quantitative studies were conducted for evaluation of CNTs using the NIOSH Method 5040 and/or electron microscopy [Maynard et al., 2004, Methner et al., 2007, Evans et al., 2010, Lee et al., 2010, Birch et al., 2011, Dahm et al., 2012].

Therefore, the purpose of this study was to establish an analytical method of determining EC in CNTs and CNFs and workplace monitoring. Specific aims of this study were to: 1) set up the analytical methods for determining EC according to the types of CNTs and CNF, 2) evaluate the correlation between EC and the metrics measured by real-time monitors, and 3) measure the CNT at workplaces in Korea.

2. Materials and Methods

2.1. The outline of this study

The outline of this study is shown in Figure 1 and consists of three stages. The first is to establish the proper analytical method for EC in CNT. The second stage is to evaluate the relationship between EC levels and metrics measured by real-time monitoring devices in exposure chamber experiments. The final stage is the exposure assessment of the workplaces in Korea. The establishment of an analytical method stage was based on domestic bulk samples (SWCNT, CNF and MWCNT) which were purchased in this study. Exposure chamber experiment used this same domestic MWCNT. The workplace monitoring stage used MWCNT which were manufactured or handled at each site.

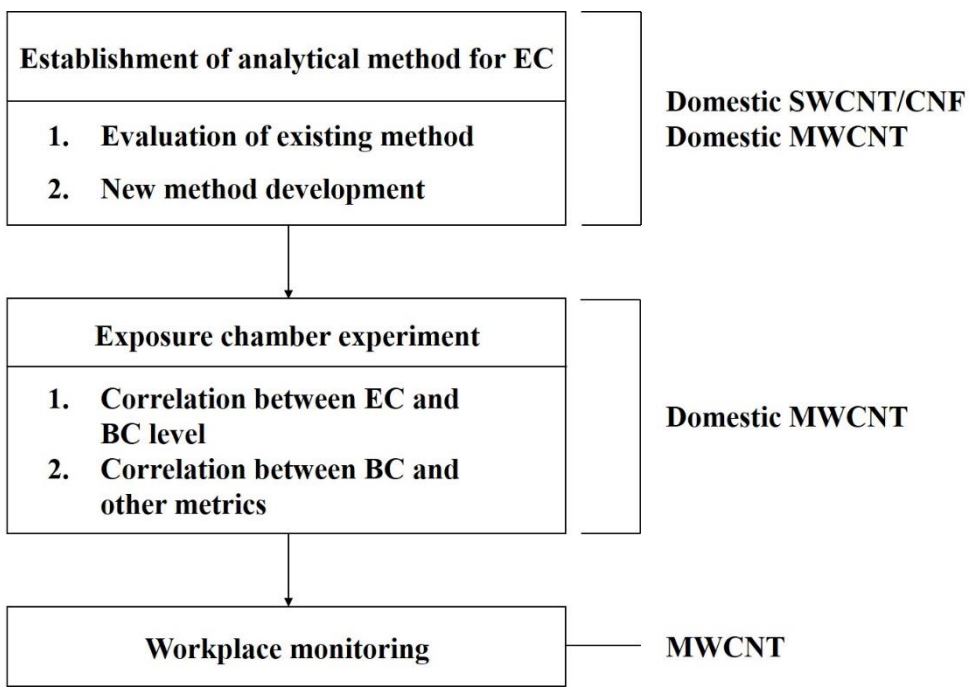


Figure 1. The outline of this study.

2.2. Establishment of EC analysis

2.2.1. CNT selection

The domestic companies which are producing and applying carbon nanotubes were selected. There are nine manufacturers for carbon nanotubes in Korea, which are Kumho Petrochemical Asan Factory; Hanwha Chemical Co., LTD; Hyosung R&D Labs; JEIO Co., LTD; CNT Co., LTD; Carbon nano-materials Technology Co., LTD; KH Chemicals Co., LTD; LG (Pilot facilities); and Samsung SDI (Pilot facilities). Among these manufacturers, seven companies have been producing carbon nanotubes for sale.

The MWCNTs that were selected were rated as industrial grade. SWCNTs and CNFs that were selected were also industrial grade, but in situations where the industrial grade materials were not available, the materials containing impurities were selected as substitutes. This is because that it was intended to electron microscopy analysis. Samples for FE-SEM(field emission scanning electron microscope, MERIN-COMPACT, ZEISS, Germany) analysis were used to assess the bulk of MWCNTs, SWCNTs, and CNF directly.

2.2.2. Sample preparation and analysis

The experiment for establishment of analytical method was performed by Guidelines for Air Sampling and Analytical Method Development and Evaluation [NIOSH, 1996]. Based on these guidelines, we made evaluations while considering recovery, limit of detection, stability, precision, and accuracy. The recovery was evaluated by calculating recovery rate by types of each analytical method. Limit of detection was considered by preparing a lower range of concentration of CNTs (1-10 μg), which was near the limit of detection**.** Stability of the samples was refer to several studies to CNTs has a tendency in thermal and chemical stability[Yano K, et al., 1997]. The accuracy and precision were used to measure the consistent degree between the measured value and the theoretical value by calculation of mean, standard deviation, and pooled standard deviation.

According to the NIOSH Method 5040 method, thirty-seven mm quartz filters (Type R-100, SKC Inc., USA) were pre-heat treated (900 ℃, two hr) in order to decrease organic carbon contamination using an electric furnace (WiseTherm, Daehan Scientific, Korea). Using CNTs and CNF bulk, samples were directly weighed (XP6 microbalance, one μg sensitivity, Mettler-Toledo, Switzerland) on a punched pre-treated quartz filter for 1.5 cm^2 area, which is usually used in analyzing by Carbon monitor(thermal/optical aerosol carbon analyzer, Sunset Laboratory, USA). The range of CNTs and CNF were from one to ten μg. These samples are analyzed by each methods as shown below (Table 1). The result of the analysis was used to calculate the recovery rate, taking into account the purity of the samples. In thermal analytical methods, a punched quartz fiber filter samples is

thermally treated in helium atmosphere, then oxygen is added to the atmosphere to oxidize the carbon component. During carbon analysis, organic carbon (OC) and EC amounts are mainly determined without oxygen and with oxygen, respectively.

In this study, six different thermal analysis protocol were applied: (1) NIOSH Method 5040; (2) Modified NIOSH Method 5040; (3) Modified IMPROVE A protocol; and (4)-(6) protocol 1-3, respectively. Table 1 summarized the detailed description of each protocol. NIOSH Method 5040 was developed for evaluation of EC in diesel particulate matter. Modified NIOSH method 5040 was adjusted for temperature and duration in the final step of the analytical program from 870 ℃ for 120 s to 930 ℃ for 120 s. Modified IMPROVE A protocol was used in determining evaluation of organic carbon (OC) and EC in environment. Protocol 1, protocol 2, and protocol 3 (Table 1) were slightly modified to the Modified NIOSH Method 5040, and each was modified the duration time of EC analysis stage. Table 1 summarizes the detailed description of each protocol.

Table 1. Analytical conditions of the six methods used in this study

Carrier gas	NIOSH 5040		Modified NIOSH 5040		Modified IMPROVE Protocol		Protocol 1		Protocol 2 (New method for MWCNT)		Protocol 3	
	Temp. (℃)	Time (s)	Temp. (℃)	Time (s)	Temp. (℃)	Time (s)	Temp. (℃)	Time (s)	Temp. (℃)	Time (s)	Temp. (℃)	Time (s)
He	1	10	1	10	1	10	1	10	1	10	1	10
	310	80	310	80	120	180	310	80	310	80	310	80
	475	80	475	80	250	180	475	80	475	80	475	80
	615	80	615	80	450	300	615	80	615	80	615	80
	870	110	870	110	550	300	870	110	870	110	870	110
	550	45	550	45			550	45	550	45	550	45
2% O_2/He	550	45	550	45	550	360	550	67.5	550	90	550	112.5
	625	45	625	45	700	600	625	67.5	625	90	625	112.5
	700	45	700	45	920	360	700	67.5	700	90	700	112.5
	775	45	775	45			775	67.5	775	90	775	112.5
	850	45	850	45			850	67.5	850	90	850	112.5
	870	110	870	60			870	90	870	120	870	150
			930	120			930	180	930	240	930	300
Total		860		930		2,400		1,012.5		1,215		1,417.5

2.3. Exposure chamber experiments

2.3.1. Aerosolization of CNT

Among obtained MWCNTs, we selected a MWCNT which is easily dispersed than others. A 1.0 mg/200 mL 90% MWCNT suspension was prepared using distilled water and was sonicated for three hours at 60 ℃. Thee dispersion of MWCNTs was relatively stable in three hours with ultrasonic bath in a previous study [Ahn et al., 2011]. CNT suspension were generated by drawing compressed air (KC65110, KOHANDS CO., Korea) through a high-efficiency particle air (3074B, TSI Inc., USA) filter into a Collison nebulizer (Nebulizer, Model CN-25L, BGI, USA) operating at thirty psi.

2.3.2. Sampling and analysis

The sampling was performed by both real time sampling and integrated sampling.

Real-time sampling

The instruments for real time monitoring were used by metrics including particle number concentration, size distribution, mass concentration and surface area concentration. Scanning Mobility Particle Sizer (SMPS, Nanoscan, Model 3910, TSI Inc., Shoreview, MN, USA) and Optical Particle Sizer (Model 3330, TSI Inc., Shoreview, MN, USA) were used to monitor particle size distribution in real time. The detectable size ranges of the instruments were from 10 to 420 nm for SMPS, and 300-10,000 nm for OPS, respectively. The total number concentration from 20 to 1,000 nm was measured using a condensation particle counter (CPC, P-

Trak, Model 8525, TSI Inc., Shoreview, MN, USA).

A DustTrak (DRX aerosol monitor model 8533, TSI Inc., USA) with a size range of 0.1 to 15 µm was used to measure the mass concentration. To measure the surface area concentration, a surface area monitor (SAM: AeroTrak Model 9000, TSI Inc., Shoreview, MN, USA) was used. The measuring particle size range was 10 to 1,000 nm, and the aerosol concentration range was 1 to 10,000 $\mu m^2/cm^3$ for the alveolar deposition method. The Aethalometer (MicroAeth® Model AE51, AethLabs, San Francisco, CA) was used to measure BC air concentrations using light emitting diodes (LEDs) at 880 nm. In case of CPC, DustTrak, and SAM, the zero calibration was performed using a HEPA filter before sampling before sampling. The interval of all real time monitors in this study was set to one minute.

Integrated sampling

Two types of collecting media were used, a thirty-seven mm quartz fiber filter (225-1824, Lot# 12158-7DBPASK-052, SKC Inc., USA) for carbon analysis and a polycarbonate membrane filter (37 mm, 0.4 µm, SKC Inc., USA) for the Scanning Electron Microscope (SEM) analysis. Samples were collected using open-face three piece cassettes and air was pulled through these cassettes at four Liters/minute using the Aircon-2 (Gilian, USA) pump and two L/min using the AirChek (SKC, USA) pump for quartz fiber filter and polycarbonate filter, respectively. Quartz fiber filters were pre-heat treated in order to decrease organic carbon contamination. For support quartz pads, a double-layer quartz filter was used to decrease organic carbon contamination. A mini particle sampler (MPS, INERIS, France) with TEM copper mesh grid (Quantifoil ® R 1/2 200 mesh) was

used to measure airborne CNTs morphologies and particle sizes using a high volume pump (Escort ELF, MSA, USA) at a constant flow rate of 0.8 L/min. After sampling, the whole samples were kept in a desiccator in a weighing room (Temp 20±1 ℃, RH 50±5%).

Whole exposure chamber experiments protocol is shown in Appendix 1.

2.4. Exposure assessment in workplaces

2.4.1. Site descriptions

There are nine manufacturers including two pilot facilities in Korea. However, there is limited access to the inside of the workplaces because these facilities handle extensive patent technology and trade secrets in manufacturing or handling CNTs. Therefore, we selected one workplace and one laboratory.

Site A was a primary manufacturing facility for MWCNTs. This MWCNT production was run continuously each week. The processes sampled at Site A included workplace cleaning, making of solutions, catalyst production, producing MWCNTs, packing (operating & maintenance), and QA/QC. The process of making solutions was performed every one or two months, and catalyst production process mixing these solution with various heavy metals. This process involved a sampling process for QA/QC of the catalyst every two hours. In the manufacturing CNT process, chemical vapor deposition (CVD) is used to produce MWCNTs in a large reactor. This process involved a sampling process for QA/QC of MWCNTs every twelve hours. The final packing operation was divided in two parts. One was made in the form of pellets and the other is packing power directly. This process was conducted using a conveyor belt with exhaust ventilation. The final stage of this process, which is packing MWCNTs in vinyl was handled directly by workers. The office is located to the same floor with the production area.

Site B was a material engineering laboratory and the secondary manufacturer of MWCNTs. The processes sampled at Site B included weighing and sonicating of several grams of MWCNTs on an open table. First, workers performed experiments weighing epoxy and MWCNTs, respectively, and then mixing them. After mixing, sonicating using ultra-sonication for one hour. This process was performed one or two times in a week; weighing, mixing, and sonicating was repeated once or twice every cycle. In the office, workers perform research desk work.

Exposure measurement at the office area were taken to study potential secondary exposure coming from the production area. Both office area not connected to the production or handling area.

2.4.2. Sampling and analysis

This sampling and analysis for monitoring workplaces was identical to the method described in 2.3.2. The schematics of each sampling sites are shown in Appendix 2.

2.5. Statistical analysis

The results of three repeated analyses by recovery rate experiments are expressed as means±standard deviation. Also, pooled relative standard deviation (Sr_{pooled}) is calculated for determining the degree of precision. The equation of recovery and pooled relative standard deviation are as shown below.

$$\text{Recovery rate, \%} = \left\{\left[\left(\frac{Amount\ of\ analyzed}{Amount\ of\ additives}\right) \times 100\right] \div purity\right\} \times 100$$

$$Sr_{pooled} = \sqrt{\frac{(N_1 - 1){Sr_1}^2 + (N_2 - 1){Sr_2}^2 + \cdots + (N_n - 1){Sr_n}^2}{(N_1 - 1) + (N_2 - 1) + \cdots + (N_n - 1)}}$$

The data indicated log-normal distribution from the Shapiro-Wilk test, so the geometric mean (GM) and geometric standard deviation (GSD) of the number concentration, surface area concentration, and mass concentration were calculated for the descriptive statistics. All the data were positively skewed, therefore all of real-time monitoring data were adapted to a log-normal distribution. For comparison between EC Concentration and real-time monitoring devices are

analyzed by Pearson correlation. The Pearson correlation coefficient was calculated to analyze the relationship among the level of EC concentration and real-time monitoring metrics including BC concentration measured by Aethalometer, SMPS, CPC, OPC, SAM, and DustTrak. Correlation was analyzed with a statistical significance at α =0.05. SAS 9.4 (SAS Institute Inc., USA) and Sigmaplot 10.0 (Systat Software, Inc., USA) were used to process the data analysis.

3. Results

3.1. Characteristics of selected materials

A total of seven carbon nanotube materials in four companies purchased from the internet were investigated. Purchased materials were three SWCNTs from two manufacturers, one CNF, and three MWCNTs from three manufacturers. The tested CNTs and CNF materials, which were purchased from manufacturers, are listed in Table 2. Also, from the SEM/EDS results, each samples had a different diameter and length, as shown in Appendix 2.

Table 2. List of tested CNT and CNF materials

Type	Manufacturer	Purity (%)	Length (μm)	Outside diameter (nm)
MWCNT 1	Carbon Nano-material Technology Co.	90	<10	5-20
MWCNT 2	Hyosung R&D Labs	95	20-30	15 (mean)
MWCNT 3	Hanwha Chemical Co.	90	-	10-15
SWCNT 1	Carbon Nano-material Technology Co.	95	<10	1-2
SWCNT 2	KH Chemicals Co.	20	-	-
SWCNT 3	KH Chemicals Co.	60	-	-
CNF	Carbon Nano-material Technology Co.	90	10-30	50-300

3.2. Recovery rate experiments results

The recovery rate of different analytical methods for SWCNT & CNF is shown in Table 3. The data of total recovery rate showed that all types of analytical methods were greater than 97%. The recovery rate and standard deviation obtained from NIOSH Method 5040 were 92.8±1.2%, 101.0±4.6%, 93.8±2.1% for SWCNT, and 103.4±3.2% for CNF. The total recovery rate and pooled standard deviation were calculated for 97.7±5.4% and 0.0012. When using Modified NIOSH Method 5040, the recovery rate and standard deviation were calculated for 95.8±3.4%, 106.1±3.2%, 95.9±3.1% for SWCNT, and 106.9±2.8% for CNF. The total recovery rate and pooled standard deviation were 101.2±6.2% and 0.0013. Similarly, The results obtained from Modified IMPROVE A protocol were 101.3±6.3%, 107.2±3.5%, 100.7±5.1% for SWCNT, and 110.3±1.0% for CNF. The total recovery rate and pooled standard deviation were calculated for 104.6±5.7% and 0.0025. Modified NIOSH Method 5040 and Modified IMPROVE A protocol shows a similar results in higher recover rate and pooled standard deviation than NIOSH Method 5040. Based on the results of experiments, the NIOSH Method 5040 is effective for analyzing SWCNT & CNF with consistent recovery rate and pooled standard deviation.

Table 3. Results of recovery rate by types of analytical method for SWCNT and CNF

Protocol	Test	SWCNT 1	SWCNT 2	SWCNT 3	CNF
		Recovery rate±Standard deviation (SD) (%)			
NIOSH 5040	Test 1	92.3	100.3	92.3	100.0
	Test 2	91.9	105.9	92.9	106.5
	Test 3	94.3	96.8	96.1	103.4
	Mean±SD	92.8±1.2	101.0±4.6	93.8±2.1	103.4±3.2
	Total, Sr_{pooled}	97.7±5.4, 0.0012			
Modified NIOSH 5040	Test 1	98.8	107.2	98.9	109.9
	Test 2	92.2	102.5	96.1	106.4
	Test 3	96.4	108.6	92.6	104.4
	Mean±SD	95.8±3.4	106.1±3.2	95.9±3.1	106.9±2.8
	Total, Sr_{pooled}	101.2±6.2, 0.0013			
Modified IMPROVE A protocol	Test 1	102.3	109.8	99.2	109.9
	Test 2	94.0	103.2	96.6	111.1
	Test 3	105.7	108.6	106.4	109.8
	Mean±SD	101.3±6.3	107.2±3.5	100.7±5.1	110.3±1.0
	Total, Sr_{pooled}	104.6±5.7, 0.0025			
Range of sample concentrations: 1-10 µg CNT /1.5 cm^2 quartz filter					

Sr_{pooled}: pooled relative standard deviation

Table 4 summarizes the results of recovery rate of MWCNT by types of existing analytical methods. The recovery rate and standard deviation obtained from NIOSH Method 5040 were 87.7±3.6%, 95.5±5.3%, 92.7±2.5%. The total recovery rate and pooled standard deviation were calculated for 91.9±4.9% and 0.0006. When using Modified NIOSH Method 5040, the recovery rate and standard deviation were calculated for 93.1±2.9%, 94.2±4.2%, 93.4±1.4%. The total recovery rate and pooled standard deviation were 93.5±2.7% and 0.0003. Simillary, The results obtained from Modified IMPROVE A protocol were 105.1±3.0%, 106.6±2.6%, 107.1±1.4%. The total recovery rate and pooled standard deviation were 106.3±2.8% and 0.0003. Overall, three existing analytical method obtained inconsistence recovery rate and standard deviation for analyzing MWCNT. As a result, among the existing analytical method, Modified NIOSH Method 5040 was modified to increase recovery rate(Table 5). The variable in which the modification of the analytical method was completed was the duration of time.

Table 4. Results of recovery rate by types of existing analytical method for MWCNT

Protocol	Test	MWCNT 1	MWCNT 2	MWCNT 3
		Recovery rate±Standard deviation (SD) (%)		
NIOSH 5040	Test 1	83.7	93.1	92.6
	Test 2	88.8	91.8	95.2
	Test 3	90.5	101.6	90.2
	Mean±SD	87.7±3.6	95.5±5.3	92.7±2.5
	Total, Sr_{pooled}		91.9±4.9, 0.0006	
Modified NIOSH 5040	Test 1	96.2	90.1	94.8
	Test 2	90.7	93.9	92.3
	Test 3	92.2	98.5	92.9
	Mean±SD	93.1±2.9	94.2±4.2	93.4±1.4
	Total, Sr_{pooled}		93.5±2.7, 0.0003	
Modified IMPROVE A protocol	Test 1	107.1	103.7	109.3
	Test 2	101.6	107.7	109.1
	Test 3	106.5	108.4	102.9
	Mean±SD	105.1±3.0	106.6±2.6	107.1±3.7
	Total, Sr_{pooled}		106.26±2.8, 0.0003	
Range of sample concentrations: 1-10 μg CNT /1.5 cm^2 quartz filter				

Sr_{pooled}: pooled relative standard deviation

Table 5 shows recovery rate results of MWCNT by analytical methods (protocols 1-3). Total recovery rate and pooled standard deviation of protocol 1 and protocol 3 were calculated for 97.2±2.8% (0.0025) and 99.1±3.9% (0.0017), respectively. When using protocol 2, which was the new method for MWCNT, the total recovery rate (pooled standard deviation) was observed to increase for 99.4 ± 5.2% (0.0028). Figure 3 shows the results of sensitivity tests by each protocol method for MWCNT. Protocol 2 and protocol 3 shows a similar recovery rate and pooled standard deviation. However, protocol 2 comes closer to the 100% recovery rate compared with protocol 3 and has the benefit of decreasing analytical duration.

Table 5. Results of recovery rate by types of modified analytical method for MWCNT

Protocol	Test	MWCNT 1	MWCNT 2	MWCNT 3
		Recovery rate±Standard deviation (SD) (%)		
Protocol 1	Test 1	92.2	101.6	96.0
	Test 2	97.8	98.9	95.2
	Test 3	99.6	95.8	97.4
	Mean±SD	96.5±3.9	98.8±2.9	96.2±1.1
	Total, Sr_{pooled}		97.2±2.8, 0.0025	
Protocol 2 (New method for MWCNT)	Test 1	100.3	104.6	95.5
	Test 2	101.3	96.6	90.1
	Test 3	96.0	106.6	103.4
	Mean±SD	99.2 ± 2.8	102.7 ±5.3	96.3 ± 6.7
	Total, Sr_{pooled}		99.4 ± 5.2, 0.0028	
Protocol 3	Test 1	102.2	95.0	102.8
	Test 2	102.5	102.4	94.7
	Test 3	96.9	101.8	93.9
	Mean±SD	100.6±3.1	99.7±4.1	97.2±4.9
	Total, Sr_{pooled}		99.1±3.9, 0.0017	
Range of sample concentrations: 1-10 µg CNT /1.5 cm^2 quartz filter				

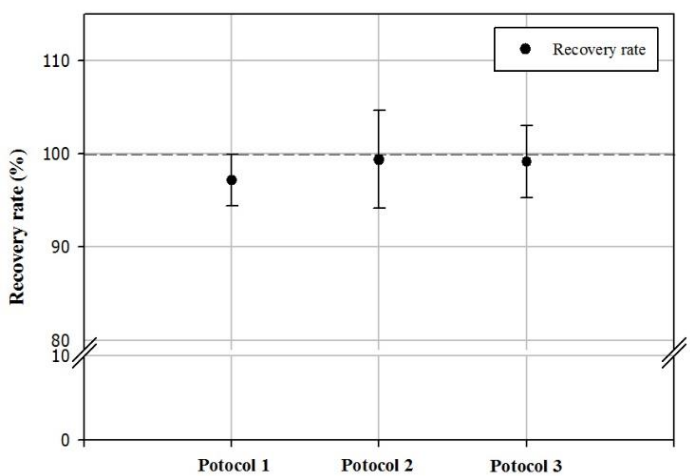


Figure 2. Results of sensitivity test by each analytical method (protocols 1-3) for MWCNT.

3.3. Confirmation of new method in other laboratory

Table 6 summarizes the result of confirming a new method in the laboratory of the Occupational Lung Diseases Institute, Korea Worker's Compensation and Welfare Service. When using the new method for MWCNT, the recovery rate were showed as 100.0%, 90.6%, 94.4%, 100.0%, and 91.1%, respectively. The mean of recovery rate and standard deviation were 95.2±4.5%.

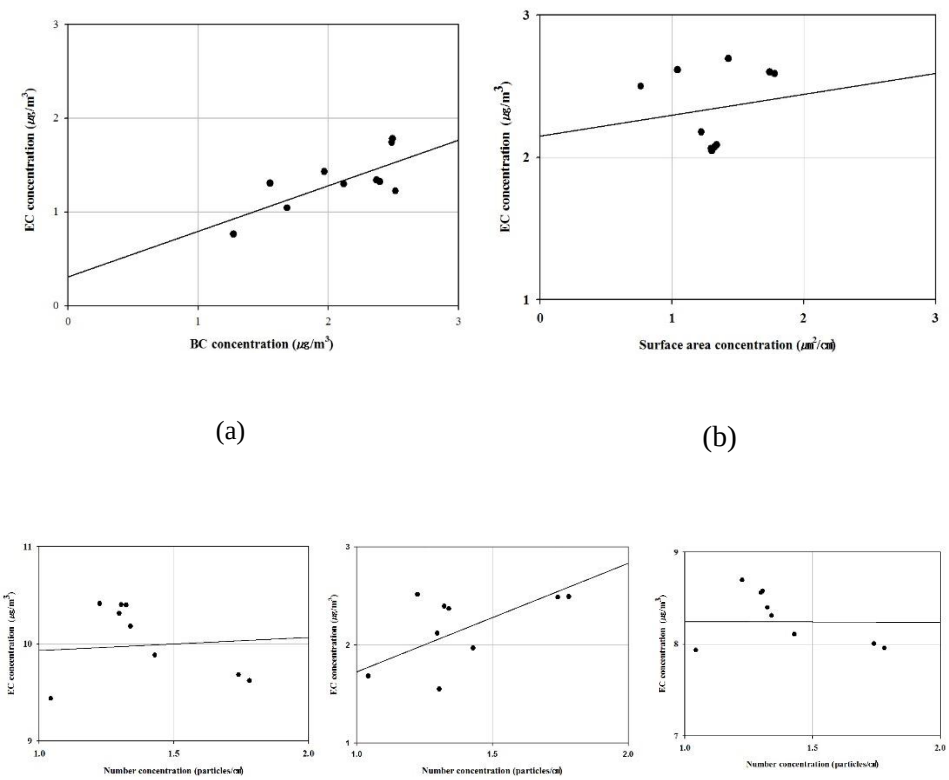
Table 6. The result of confirmation of the new method in other labs

Protocol	MWCNT 1				
	Recovery rate±Standard deviation (SD) (%)				
	Test 1	Test 2	Test 3	Test 4	Test 5
New method	100.0	90.6	94.4	100.0	91.1
Mean±SD	95.2±4.5				

Range of sample concentrations: 1-10 μg CNT /1.5 cm^2 quartz filter

3.4. Correlation between EC and real-time monitoring

Figure 4 shows a correlation graph among level of EC and real-time monitoring devices (Aethalometer, SAM, SMPS, CPC, and OPC) during exposure chamber experiments. Figure 4 (a) shows the relationship between EC level and BC level measured by Aethalometer (Pearson correlation coefficient was 0.73). Figure 2 (b) shows the relationship between EC level and surface area (Pearson correlation coefficient was 0.16). Similarly, Figure 2 (c)-(e) shows the relationship between EC level and number concentration by OPC, SMPS, and CPC (Pearson correlation coefficients were 0.10, -0.06, and -0.02, respectively). From the results, EC concentration relatively correlated with the BC concentration measured by Aethalometer and Surface area monitoring.



(a) (b)

(c) (d) (e)

Figure 3. Correlation among EC level and real-time monitors ((a) EC-BC measured by Aethalometer, (b) EC-SAM, (c) EC-OPC, (d) EC-SMPS, (e) EC-CPC).

3.5. Exposure assessment of workplaces

Table 7 summarizes the general characteristics of workplaces investigated based on the region, workplace type, types of CNTs, processes, ventilation type, number of workers, and PPE use.

Site A was a manufacturer located at Asan in Korea. A total of five process were divided into cleaning, making solution, making catalyst, manufacturing CNTs (CVD), and packing. This site installed natural ventilation (NV) and local exhaust ventilation (LEV). A total of seven workers were in an office, and four workers were handling CNTs directly. Site B was laboratory in Seoul where, weighing and sonication processes were performed. Only NV was installed and total of fifteen workers including five workers directly handling CNTs were performed in this laboratory. All the workers in site A and B were wearing a gloves and a half-mask.

Table 7. Characteristics of workplaces

Site	Region	Workplace type	Types of CNTs	Process	Ventilation type	Number of workers (CNT handling workers)	PPE use
Site A	Asan	Manufacturer	MWCNT	Cleaning, Making solution, Making catalyst, Manufacturing CNTs (CVD [a)]), Packing	NV [b)], LEV [c)]	7 (4)	Half-mask, glove
Site B	Seoul	Laboratory	MWCNT	Weighing, Sonication	NV [a)]	15 (5)	Half-mask, glove

[a)] CVD= Chemical vapor deposition
[b)] NV= Natural ventilation
[c)] LEV= Local exhaust ventilation

Table 8. Summary statistics of workplaces by process and monitoring devices

Workplace		EC concentration ($\mu g/m^3$)	GM (GSD) [5th-95th percentile]								
			SMPS (particles/cm^3)			OPC (particles/cm^3)		CPC (particles/cm^3) (20-1,000 um)	SAM ($\mu m^2/cm^3$) (10-1,000 um)	DustTrak (mg/m^3) (0.1-15 μm)	Aehtalo-meter (ng/m^3) (880 nm)
			Total number Concentration (11-420 nm)	≤ 100 nm	> 100 nm	Total number Concentration (300-10,000 nm)	≤ 0.3 μm				
Site A	Cleaning	4.98±3.39 (N=3)	12,228 (1.07) [10,367-13,265]	9,680 (1.09) [8,169-10.988]	2,524 (1.11) [2,133-2,938]	78.62 (1.04) [73.33-82.74]	70.12 (1.04) [65.51-73,77]	4,920 (1.04) [4,658-5,138]	30.13 (1.01) [25.23-33.07]	0.03 (1.06) [0.03-0.03]	992 (1.56) [587-1,619]
	B.G[a)] of Cleaning	3.57±0.45 (N=3)	11,335 (1.02) [10,617,-11,705]	8,804 (1.03) [8,236-9,110]	2,528 (1.05) [2,250-2,668]	73.02 (1.02) [71.36-74.65]	64.59 (1.02) [63.04-66.05]	4,347 (1.02) [4,035-4,499]	27.90 (1.01) [27.05-28.22]	0.03 (1.04) [0.03-0.03]	1,534 (1.10) [1,185-1,792]
	Office	2.36 (N=1)	6,691 (1.07) [6,155-7,744]	4,359 (1.10) [3,928-5,288]	2,325 (1.07) [2,098-2,587]	114.77 (1.11) [101.00-136.58]	104.71.11) [92.67-123.88]	-	21.02 (1.10) [18.97-26.23]	-	618 (1.30) [378-835]
	Packing (P.M)	11.41±2.62 (N=3)	11,315 (1.06) [10,442-12,178]	7,773 (1.06) [7,139-8403]	3,538 (1.07) [3,219-4,030]	728.05 (1.02) [702.95-750.64]	502.13 (1.03) [482.83-529.62]	8,943 (1.05) [8,213-9,495]	75.70 (1.03) [72.59-79.62]	0.27 (1.04) [0.25-0.28]	1,906 (1,29) [1,518-2,664]
	Making solution	<LOD* (N=3)	8,867 (1.09) [7,875-10.172]	5,752 (1.12) [4,843-6,838]	3,106 (1.05) [2,861-3,403]	706.57 (1.02) [686.77-727.98]	706.12 (1.02) [507.63-542.12]	7,227 (1.10) [6,268-8,158]	67.31 (1.05) [62.85-72.54]	0.23 (1.03) [0.22-0.24]	1,616 (1.22) [1,211-2,228]
	Making catalyst	1.21±0.52 (N=3)	7,562 (1.04) [7,313-7,854]	4,574 (1.04) [4,346-4,865]	2,986 (1.03) [2,824-3,139]	751.38 (1.01) [737.66-766.33]	563.02 (1.01) [552.89-574.05]	5,943 (1.03) [5,578-6,233]	64.28 (1.01) [63.06-65.41]	0.24 (1.01) [0.24-0.24]	1,425 (1.25) [964-1,992]
	Manufacturing CNTs	6.78±2.82 (N=3)	8,212 (1.17) [7,348-11,793]	4,799 (1.23) [4,137-7,707]	3,394 (1.09) [3,109-4,073]	858.38 (1.02) [843.93-879.94]	635.91 (1.01) [625.04-650.23]	6,254 (1.11) [5,687-8,016]	71.64 (1.07) [68.48-84,08]	0.28 (1.03) [0.28-0.30]	1,428 (1.12) [1,199-1,707]
	Packing (P.M & working)	14.24±0.41 (N=3)	18,182 (1.16) [13,653-23,688]	13,725 (1.20) [10,017-20,129]	4,370 (1.17) [3,596-5,614]	916.68 (1.03) [862.37-944.53]	674.23 (1.03) [636.50-693.74]	14,001 (1.16) [10,788-19,201]	104.20 (1.10) [85.60-117.16]	0.31 (1.04) [0.29-0.33]	1,878 (1.19) [1,482-2,403]
	QA/QC	<LOD* (N=1)	14,425 (1.11) [12,842-17,100]	11,421 (1.13) [9,985-13,794]	2,990 (1.08) [2,701-3,362]	702.58 (1.08) [644.62-810.52]	569.65 (1.07) [628.13-648.01]	-	39.19 (1.05) [36.99-42.29]	-	3,623 (1.60) [1,782-6,086]

	Office	3.69 (N=1)	8,312 (1.23) [6,252-11,426]	4,833 (1.30) [3,284-6,995]	3,452 (1.14) [2,932-4,462]	765.97 (1.04) [726.25-834.69]	592.09 (1.05) [554.38-648.50]	-	36.49 (1.34) [26.47-62.33]	-	4,022 (1.39) [2,825-6,496]
Site B	Pre-B.G of workplace	0.95±0.03 (N=3)	268,282 (1.22) [206,704-401,354]	256,671 (1.23) [194,496-386,677]	9,934 (1.72) [3,899-401,354]	98.06 (1.15) [82.40-123.76]	91.36 (1.15) [76.61-115.55]	197,493 (1.15) [164,750-247,908]	552.82 (1.15) [440.79-673.96]	0.05 (1.17) [0.04-0.07]	732 (1.06) [674-814]
	Weighing & Sonicating	4.49±1.51 (N=3)	168,844 (1.14) [149,199-220,989]	165,091 (1.13) [146,672-213,334]	3,571 (1.47) [2,050-6,653]	67.42 (1.16) [54/71-79/98]	61.56 (1.14) [50.79-70.78]	122,462 (1.19) [104,486-179,592]	336.20 (1.15) [294.54-459.14]	0.03 (1.16) [0.02-0.03]	568 (1.28) [448-875]
	Post-B.G of workplace	3.62±1.10 (N=3)	151,683 (1.08) [135,155-172,312]	148,848 (1.08) [133,406-169,121]	2,726 (1.31) [1,730-4,141]	54.49 (1.05) [51.16-57.83]	50.93 (1.04) [48.06-63.90]	99,774 (1.05) [88,196-11,2657]	294.15 (1.06) [266.36-322.43]	0.02 (1.04) [0.02-0.02]	437 (1.07) [392-489]
	Office	0.75 (N=1)	187,799 (1.32) [139,870-315,774]	182,763 (1.31) [136,716-305,115]	4,287 (1.95) [1,972-16,713]	76.80 (1.32) [58.67-123.77]	71.21 (1.32) [54.64-115.60]	-	37.37 (1.32) [30.07-65.65]	-	753 (1.38) [438-1,172]

[a)] B.G = Background

[*] <LOD indicates the level of EC concentration was under 0.3 ㎍/1.5 ㎠

Table 8 summarizes the descriptive statistics of workplaces measured using EC sampling, SMPS, OPC, CPC, SAM, and DustTrak for the measured metrics (e.g., GM, GSD, and fifth through the ninety-fifth percentiles of each concentrations).

EC concentration

A total of thirty-four EC samples (twenty-four for site A, ten for site B) were measured and analyzed. Figure 5 shows the mean of the EC concentrations including standard deviation for the different area. Most measurements were higher than the office background, and two samples were below the background level as well as the analytical LOD. Overall, site A was higher than site B, according to results, maintenance and those working in packing had the highest EC exposure levels at 14.24±0.41 $\mu g/m^3$. Maintenance at packing, manufacturing CNTs, and cleaning process were at high level in that order, each concentration was 11.41±2.61 $\mu g/m^3$, 6.78±2.82 $\mu g/m^3$, and 4.98±3.39 $\mu g /m^3$, respectively. In most of the EC samples (82%), the recommended exposure limit (REL) of one $\mu g /m^3$ for EC was exceeded. Overall, measured EC levels were higher at primary manufacturers than at secondary manufacturing sites.

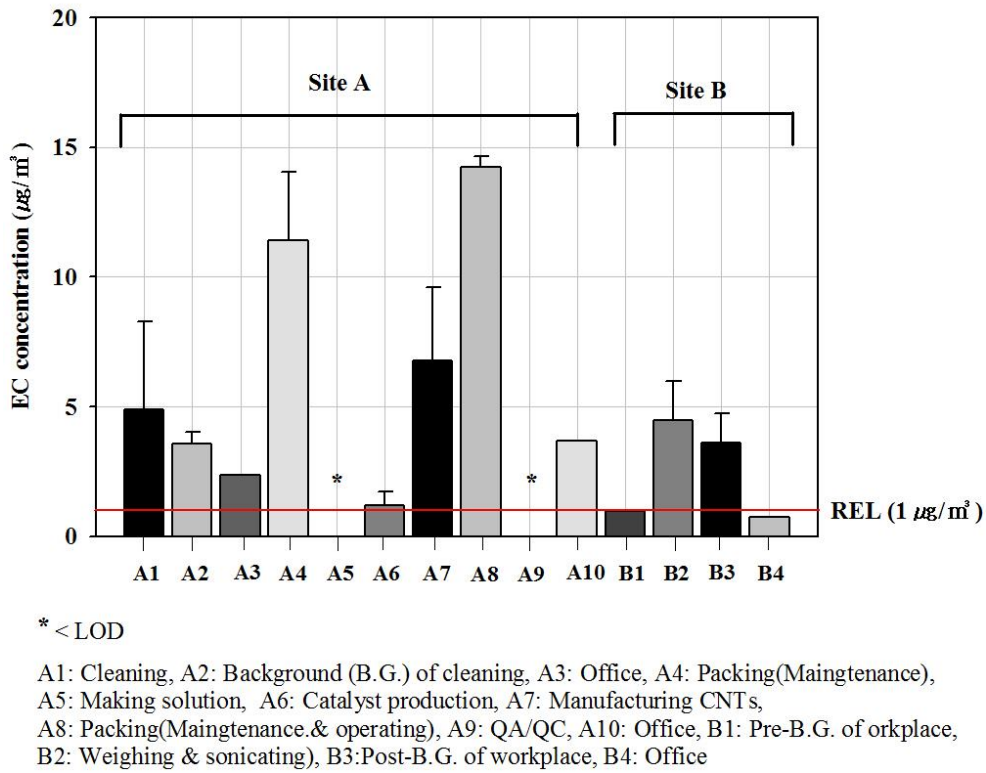


Figure 4. EC concentration measured using a quartz filter by process in workplaces (error bars indicate the standard deviation of the mean (n=3)).

Number concentration

SMPS, CPC, and OPC were used to measure for number concentration. Site A could be divided to day one (cleaning process) and day two (other process).

Site B was higher than site A in nanoparticles (<100 nm) and ranged from 1.4 x 10^4 to 4.0 x 10^4 particles/cm^3 by the SMPS. Measurement by the CPC has a similar tendency with as SMPS ranging from 8.8 x 10^4 to 2.5 x 10^5 particles/cm^3. Compared by EC level, this indicated a probable indoor nanoparticle source but did not reflect CNT exposure. In the case of measurement by OPC, site A was greater than site B, and the total concentration and under 0.3 μm in diameter particles were

collected from 644.62 to 944.53 particles/cm^3, and from 482.83 to 693.74 particles/cm^3, respectively during day two. Day one of site A was similar to the collected site B concentration.

Surface area concentration

The highest surface area observations at the packing (maintenance and working) process were 85.60 to 117.16 $\mu g/cm^3$. Also, most process during day two were higher than the indoor background concentration. The cleaning process was similar to the collected indoor background sample.

The workplace surface area concentration (266.36 to 673.96 $\mu g/cm^3$) was significantly higher than the indoor background surface area concentration (30.07 to 65.65 $\mu g/cm^3$) at site B. Among measurement in workplace, pre-background surface area in the workplace was more than surface area concentration during working hours. This could be affected by in other experiments at this workplace.

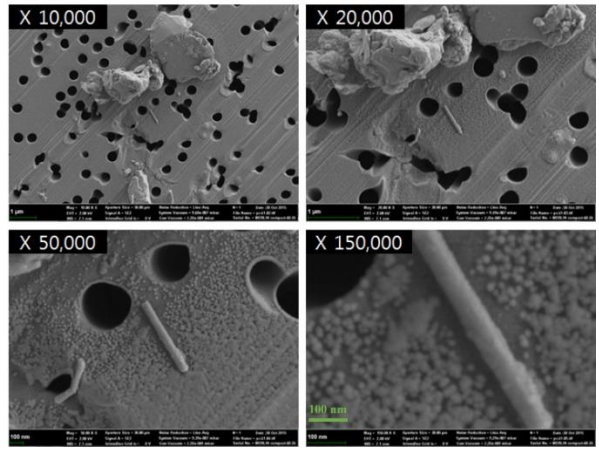
Mass concentration

The indoor background of mass concentration measured by the Aethalometer were 378 to 835 ng/m^3 at day one. During the cleaning process, the mass concentrations were 1,185 to 1,792 ng/m^3, and 587 to 1,619 ng/m^3 for workplace background during the cleaning process. The indoor background of mass concentration measured by the Aethalometer were 2,825 to 6,496 ng/m^3 at day two. The workplace mass concentration were 964 to 6,086 ng/m^3. The mass concentration measured by DustTrak were 0.03 to 0.31 during the entire process. On day two the indoor background mass concentration measured higher than production area. This is because that ultra-fine particle event occurred during the

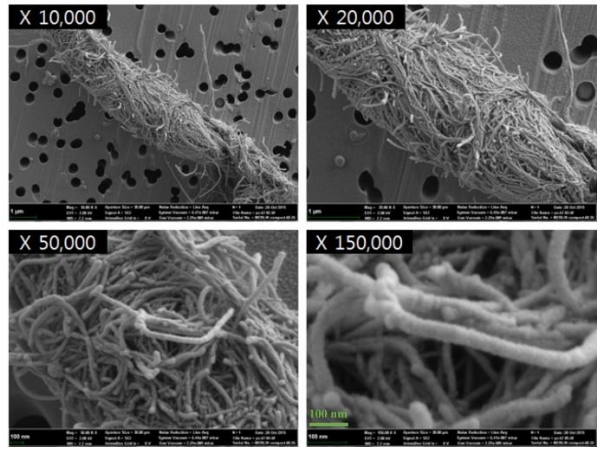
sampling day two. The indoor background of mass concentration measured by the Aethalometer was 438 to 1,172 ng/m^3, and workplace background was 392 to 814 ng/m^3 at site B. The mass concentration collected during weighing and sonicating was 448 to 875 ng/m^3. No clear exposure patterns were seen by DustTrak.

Figure 7 shows FE-SEM images collected on PC filters during (a) manufacturing CNTs in site A, (b) cleaning process in site A, and (c) weighing and sonicating process in site B. The images were magnified by 10,000, 20,000, 50,000, and 150,000, respectively. The FE-SEM images indicate that individual fibrous MWCNT particles were observed during the cleaning process in site A (Figure 7 (a)). However, agglomerates were observed in site A during maintenance at packing process in site A (Figure 7 (b)). The potential material for CNT was observed at the weighing and sonication process in site B (Figure 7 (c)), but it was not clearly distinguishable from other materials (resin).

(a)



(b)



(c)

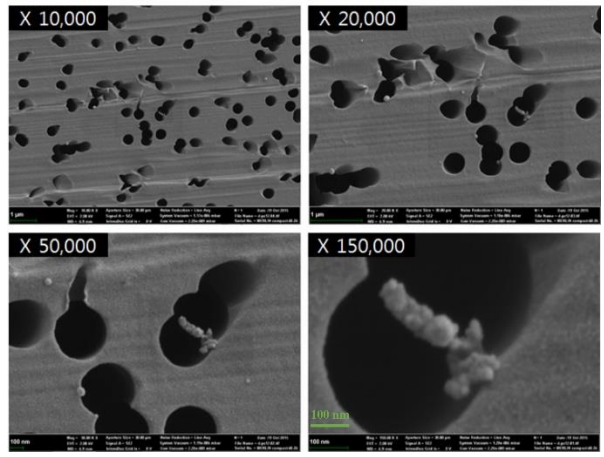


Figure 5. SEM images of workplaces ((a) cleaning process in site A, (b) maintenance at packing process in site A, (c) weighing and sonication process in site B).

4. Discussion

This study investigated recovery rate of existing analytical method for EC and airborne exposures generated during handling of the MWCNT. The results obtained by this study indicate that the effective analytical methods for EC with highly recovery rate by types of carbon nano materials. SWCNT and CNF, were effectively analyzed by NIOSH method 5040 (Table 3) and MWCNT were effectively analyzed by a new method, which was proposed in this study (Table 4, Table 5).

In this study, the six analytical methods tested in this study: NIOSH method 5040, modified NIOSH method 5040, modified IMPROVE A protocol, and protocol 1-3 were widely used for analysis of the EC and OC level in the local environment and workplaces. First, NIOSH method 5040 programmed the final step of temperature and duration were 870 ℃ for 110 seconds. When using SWCNT and CNF, the total recovery rate (pooled standard deviation) were appeared to 97.7±5.4% (0.0012), which could mean that when using NIOSH method 5040, the measured accuracy and precision of EC was effective to evaluation of SWCNT and CNF. This results were also confirmed by SWCNTs which usually start oxidation at 550 ℃ for 240 seconds and finish oxidation at 700 ℃ for 360 seconds [Ono Ogasawara et al., 2011]. On the other hand, the recovery results of MWCNT was significantly lower than the corresponding true value for 91.9±4.86% (0.0006), which indicated that the NIOSH method 5040 was needed to modify for analysis of EC in MWCNT. When using SWCNT and CNF analyzed by Modified NIOSH Method 5040, the results of recovery rate appeared

to correspond to the analysis for 101.2±6.2% (0.0013). Therefore, it can be concluded that when using NIOSH Method 5040, the measured accuracy and precision of EC in SWCNT and CNF was more effective to evaluation. Also, this method, compared to the other two methods, has benefits of a relatively short analysis time. Meanwhile, the MWCNT was not responsive to using this method. When using Modified IMPROVE A protocol, every CNT and CNF were analyzed at over 100% of recovery rate. While the other carbonaceous were detected during the final OC stage (Appendix 4), it could be detected during EC stage when using Modified IMPROVE A protocol. According to Ono Ogasawara et al. (2011), it could have a positive interference, when other carbonaceous materials are present.

Several previous proposed methods were modified to completely oxidize for MWCNTs, and to quantify the MWCNTs. This is because thick fibers— like graphite fibers— are usually oxidized at over 870 ℃. However, sometimes thick fibers are not oxidized, even at 920 ℃ [Ono Ogasawara et al., 2011]. Similarly, our proposed new methods were modified to completely oxidize of MWCNT. Also this method could a certainly distinguish of detection peak by increasing of last temperature step and extension of analysis time. Therefore, it could be concluded that when using the new method for MWCNT, the measured accuracy and precision were comparatively higher, and fit better reflected its true value

This study also confirmed the correlation between EC levels and real-time monitoring devices. The BC levels showed a relatively good correlation with EC levels, and according to an EPA report in 2012, the level of ambient BC and EC

concentration measured by Aethalometer had an average correlation coefficient of 0.86 ± 0.11. Ji et al., (2014) evaluated relatively high correlation between CNTs by EC and BC measured by Aethalometer. In our study the correlation corresponded with these studies with a correlation coefficient of 0.73. However, the mean BC level was about twofold the mean EC level in our study; and this further confirmed by other studies [Andreae & Gelencsér 2006, Jeong et al., 2004b, Jeong et al., 2008, Salako et al., 2012, Yelverton et al., 2014]. Since the Aethalometer measured only particles with 880 nm specific wavelength to BC and contained organic components in addition to EC, this may explain the differences between EC and BC [Andreae & Gelencsér 2006; Yelverton et al., 2014]. However, other real-monitoring devices are commonly used to determine particle of spheres and are not applicable for elongated particles. Therefore, this strong correlation among real-monitoring metrics could make it difficult to confirm that it is from the other particles or CNTs contribution. It can be concluded that measuring the EC and BC by Aethalometer is effective, and the other monitoring devices were difficult to utilize to monitor EC particles specifically as they only monitored the entire group of nano particles.

This study also investigated MWCNT exposure at workplaces (site A: MWCNT manufacturing facility and site B: MWCNT handling laboratory), and identified various release nano particles including MWCNT at the work processes, such as cleaning workplaces, maintenance of packing conveyor, manufacturing MWCNTs, etc. Most EC levels at workplaces were higher than REL recommended by NIOSH. However, the REL was based on respirable mass concentration. According to suggestion by Erdely et al. (2013), about 4% of TSP were estimated

for EC from their exposure data and a respirable fraction of EC was twenty-five. Therefore, 1% of total suspended particulate (TSP) could be estimated for respirable EC. Workers could be exposed to 0.01–0.14 μg/m^3 of EC in the site A and 0.01–0.06 μg/m^3 of EC in the site B, indicating that they are exposed to a low concentration compared with the NIOSH REL one μg/m^3.

Exposure to nanoparticles in most processes in this study were found to release particles into the workplace air. Similarly, previous results by Han et al. (2010), CNT handling processes including CNT preparation, opening the CNT spray cover, wafer heating, opening the water bath, and ultrasonic dispersion, were also found to release particles into the air in workplaces. However, this results could be overestimated due to ultra-fine particle issues during site A sampling. The results also showed evidence that workers could be exposed to nanoparticles during every process when the process is conducted in an imperfect exhaust duct system. The local exhaust duct system was shown to be insufficient for removing the nanoparticles released, particularly in the packing process.

This study also attempted to measure surface area concentration. Based on the results of site A, when the EC level is high, it was confirmed that SAM result also high (Table 8). This result corresponds with correlation results in the exposure chamber experiment (Figure 3). However, because of the high level of background nano-sized particle concentrations, it may be difficult to confirm the CNT contributions in site B. This result corresponds to previous studies showing that active surface area concentration appears to closely follow CNT emissions, more than mass concentrations [Heitbrink et al., 2009, Evans et al., 2010]. These observed results, mixed exposure perspective, surface area measurements may still

provide some useful information within the workplace [Evans et al., 2010, Birch, 2011].

Monitoring the black carbon concentration also provided supporting evidence of the release of MWCNTs, along with other real-time monitoring devices. In all sites, the black carbon level appeared to relatively correlate with the level of EC at the Pearson correlation coefficient for 0.27. This result shows a lower level of correlation compared with chamber test results. Measurement with the Aethalometer did not reflect a changes in emissions of CNTs and CNFs during the sampled process, most likely due to inadequate sensitivity [Dahm et el., 2012]. However, a previous study found the Aethalometer to be the most useful monitoring metri. This previous study was conducted at a location which produced and handled large quantities of CNFs [Evans et al., 2010]. Therefore, more correlative studies of EC level and Aethalometer are needed in the workplace. Measurement mass concentration by the DustTrak appeared difficult to distinguish carbon nano-materials and other particles. In addition, this monitoring device is difficult to apply for measuring carbon nano-materials due to inadequate detective range (0.1 to 15 μm).

The FE-SEM/EDX analysis of the area sampled specimens indicated various structures of airborne MWCNTs, and some particles were lager than to one ㎛, suggesting that fibers that could be ingested by lung macrophages. Maynard et al. (2004) also carried out a laboratory-based study to evaluate the physical nature of the aerosol formed from SWCNTs material during mechanical agitation, and estimated nanotube concentrations ranging from 0.7 to 53 ㎛/m^3. We think that a

scanning electron microscope analysis is necessary for identifying the CNT sources.

For field application, interpretation is further confounded by uncontrolled aerosol sources. Currently, it is unclear whether a metric other than integrated sampling is a more appropriate metric to predict human health effects due to CNTs and CNFs exposure. However, some studies found positive correlations between the integrated sampling and microscopy metrics. To sum up, in parallel work using quartz filter-based for EC, electron microscopy analysis, appear to be the most reliable, selective, and feasible way to conduct quantitative exposure assessments of workers exposed to CNTs.

Limitations

The first limitation of this study is the recovery rate in different types of analytical methods focused on the EC analysis including the direct use of CNT bulk samples. Experiments in this study had a relatively small influence on the OC due to the performance in exposure chamber. Therefore, increasing the influence of OC and TC may be inappropriate. However, field may have various sources of ambient OC. In the future, airborne CNT samples should be analyzed for EC by a new method prior to applying the exposure assessment in workplaces. Thus further studies using carbon nanotubes released from air or handling processes shoul be conducted.

Another limitation is that many real-time monitors rely on a particles' optical properties index as the basis for operation. Further, the accuracy in response to particles or fibers of irregular shape may vary [Gebhart, 1991, Umhauer & Bottlinger, 1991, Szymanski et al., 2009]. Therefore, the complex aggregates/agglomerates shapes of CNTs and CNF could result in erroneous measurements by using real-time monitors.

The Aethalometer could cause errors in measurement of BC level for several reasons. The Aethalometer has not been validated and adfusted for circumstances of rapid changes in temperature, humidity, pump flow rate, inconstancy of diode wavelength, ability of the photosensitive sensor, and adequately replaced filters. These could cause potential errors to occur in measurement. Further, if there is a significant background concentration of OC, which could affect the concentration of the BC and EC [AethLabs. 2015].

5. Conclusions

There is no standard analytical method to evaluate the CNTs and CNFs. NIOSH Method 5040 has been widely used to evaluate the CNT/CNF from elemental carbon (EC) analysis. This study focused on establishment the effective analytical methods for EC in types of CNTs and CNF. SWCNT and CNF were effective to analyzed using NIOSH Method 5040. MWCNT was effective to analyzed using a new method which is proposed in this study.

In addition, investigation of the correlation between EC concentration and real-time monitors and the correlation among real-time monitors which are widely using nanoparticle sampling devices was examined. There is a relative relationship between EC level and BC level measured by Aethalometer. EC level also has a slight correlative relationship with SAM. Therefore, EC and Aethalometer sampling may be the useful to CNT exposure assessment. However, other nanoparticle sampling devices and congruent electron microscopy analysis may be necessary for better assessing CNT exposure.

This study demonstrated significantly higher MWCNT exposure during handling of MWCNTs. Also, during the monitoring at one workplace and one laboratory, some individual or agglomerates of MWCNT were released into the air and most of the EC samples exceed the REL. Therefore, we confirmed several processes that are associated with significantly increased exposure, which will give focus to sources aimed at mitigating exposure levels to MWCNT.

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국문초록

탄소나노튜브 및 탄소나노섬유의 분석방법 설정과 이를 이용한 국내 취급 사업장 노출평가

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Ⅰ. 연구목적

탄소나노물질의 노출 평가는 열분석을 통한 원소탄소 농도로 결정할 수 있다. 그러나 열분석에 제안되는 NIOSH Method 5040은 본래 디젤 배출물을 측정하기 위한 방법이며, 현재까지 열분석 방법에 대한 신뢰성 확보에 대한 연구가 미비한 실정이다. 또한, 국내의 탄소나노물질 제조 및 사용 증가에 따른 작업장 노출평가는 현재까지도 진행 중에 있다.

따라서 본 연구에서는 국내 탄소나노물질 종류에 따른 열분석 방법을 설정하며, 공기중 측정에 있어서 원소탄소를 통한 방법과 실시간 나노입자 측정기를 이용한 분석방법의 상관성을 평가하였다. 또한, 설정된 열분석 방법과 나노입자 측정기를 이를 이용하여 국내 탄소나노튜브 취

급 사업장을 대상으로 노출평가를 실시하였다.

Ⅱ. 연구방법

탄소나노물질 종류에 따른 분석방법 설정을 위한 회수율 실험은 Guidelines for Air Sampling and Analytical Method Development and Evaluation (NIOSH, 1996)의 실험방법의 확립단계를 참고하여 평가하였다. 공기중 원소탄소와 실시간 나노입자 측정기의 상관성을 평가하기 위하여 노출 챔버 실험을 실시하였다. 원소탄소의 측정은 석영 필터를 사용하였으며, 실시간 나노 측정 기기는 Aethalometer, scanning mobility particle sizer (SMPS), condensation particle counter (CPC), optical particle counter (OPC), surface area monitor (SAM), DustTrak을 사용하였다. 또한, 채취된 CNT의 형태를 확인하기 위하여 polycarbonate 필터 및 TEM grid를 사용하여 전자현미경 분석을 하였다. 사업장 노출평가는 노출 챔버 실험과 동일한 방법으로 진행되었으며, 대상은 국내의 제조회사 한 곳과 취급 실험실 한 곳을 선정하여 평가 하였다.

Ⅲ. 연구결과 및 고찰

회수율 실험 결과, 단일벽 탄소나노튜브 및 탄소나노섬유의 NIOSH Method 5040에 따른 회수율 결과를 전체 평균 및 표준편차와 합병상대표준편차로 나타내면 97.7±5.4%, 0.0012로 나타났다. 다중벽 탄소나노튜브의 경우는 본 연구에서 제안하는 new method를 사용하여 분석한 결과를 동일하게 나타내면 99.4±5.2%, 0.0028이다. 챔버 실험을 통한 원소탄소 방법과 실시간 측정 기기간의 상관성은 Aethalometer가 가장 상관성이

높은 것으로 나타났으며(피어슨 상관 계수=0.73), SAM을 통한 측정과도 약간의 상관관계가 있는 것으로 나타났다(피어슨 상관 계수=0.16). 사업장 노출평가 결과 전체의 82%가 NIOSH의 REL 기준치를 초과하는 것으로 나타났다.

Ⅳ. 결론

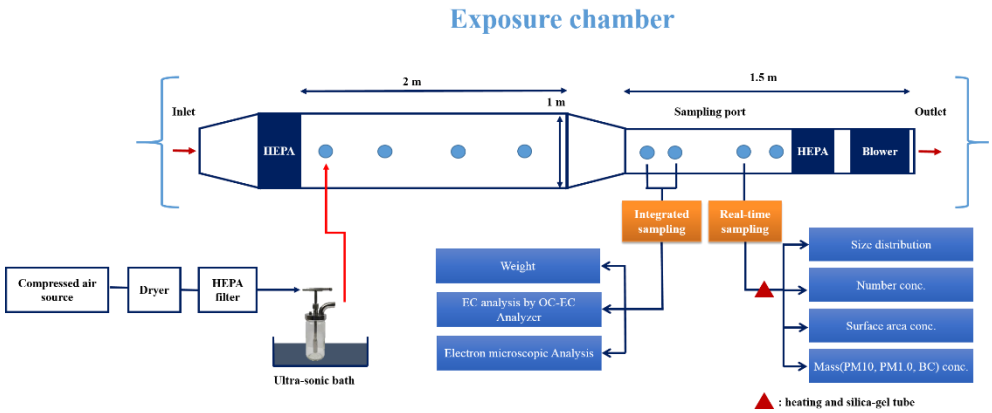
단일벽 탄소나노튜브 및 탄소나노섬유의 열분석 방법은 NIOSH Method 5040이 적절하며, 다중벽 탄소나노튜브는 본 연구에서 제안하는 New method가 적절하다. 공기 중 탄소나노물질의 노출평가를 위해서는 원소탄소로 평가되어야 하며, 동시에 원소탄소와 상관성을 보이는 Aethalometer를 이용한 측정 및 전자현미경 분석이 병행되어야 한다. 또한, 국내 사업장 노출평가 결과 대부분의 원소탄소 샘플이 기준치를 초과하는 결과를 나타내어 노출 저감 관리가 필요할 것으로 보여진다.

주요어: 탄소나노튜브, 탄소나노섬유, NIOSH Method 5040, 원소탄소, 사업장 노출평가

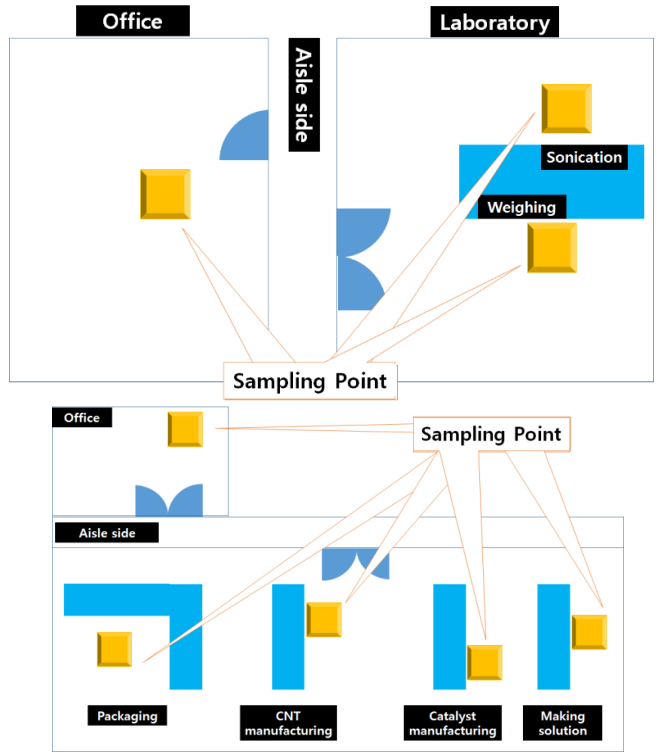
학번: 2014-23363

Appendices

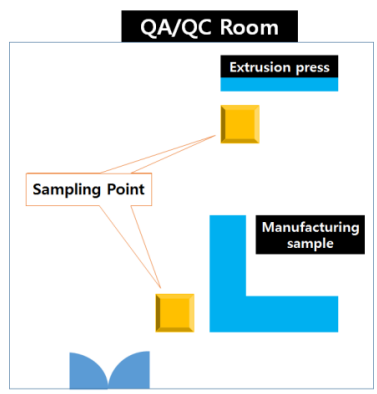
Appendix 1. The diagram of the exposure chamber experiment



Appendix 2. The **s**chematic of sampling site B (a) workplace for CNT manufacturing (b) QA/QC room.

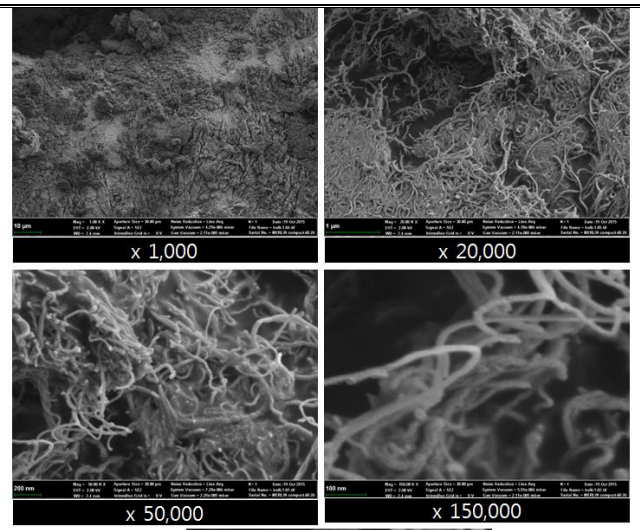
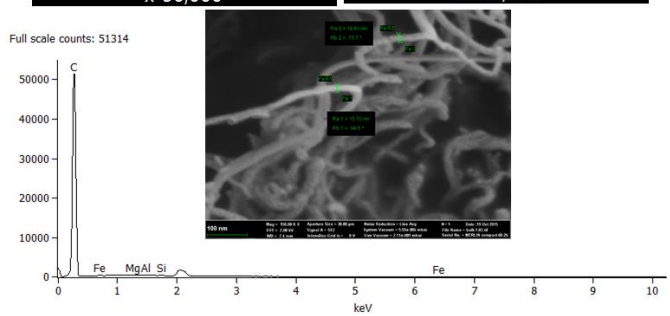


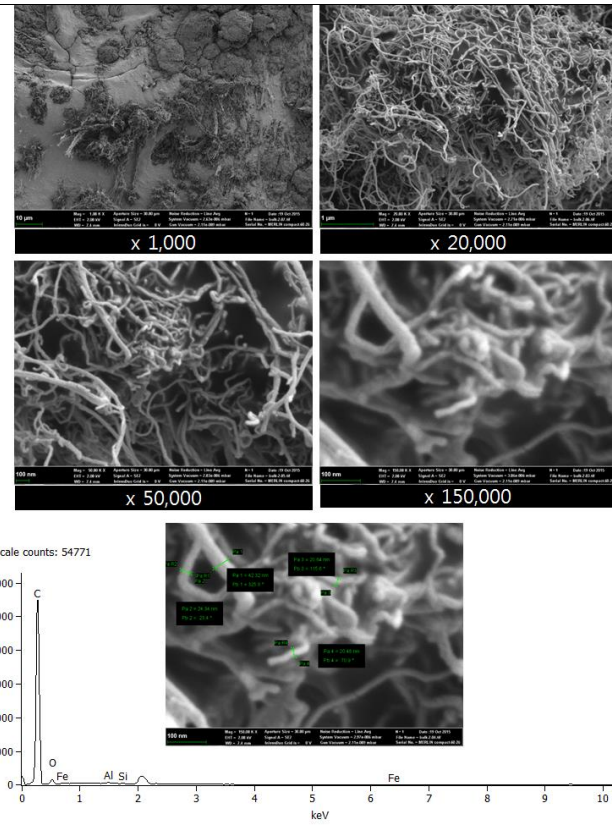
(a)

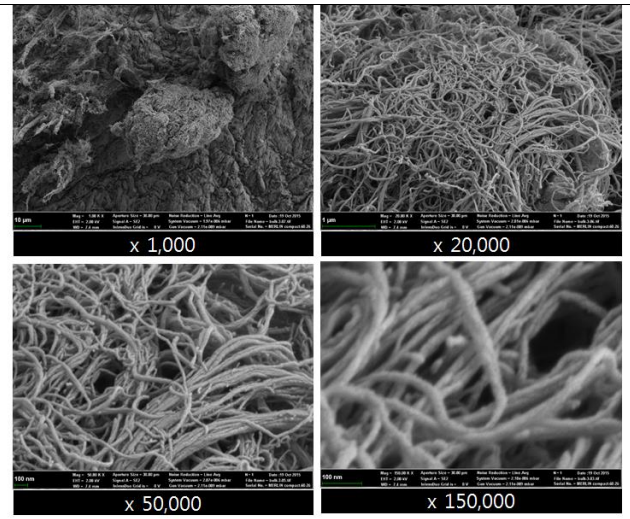
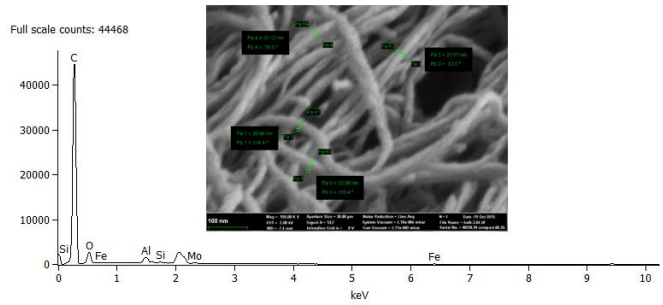


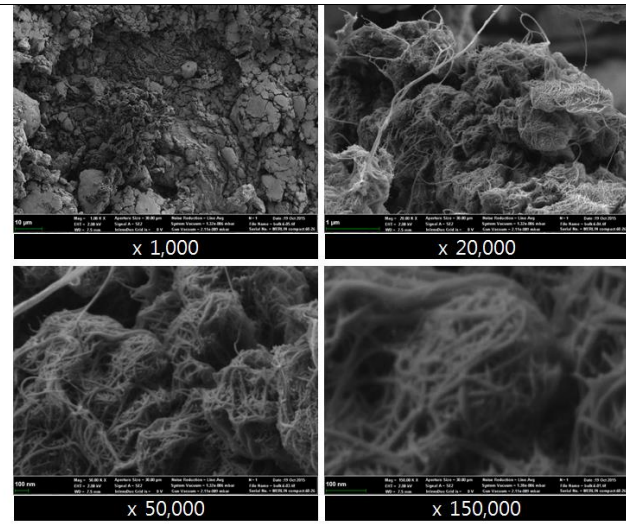
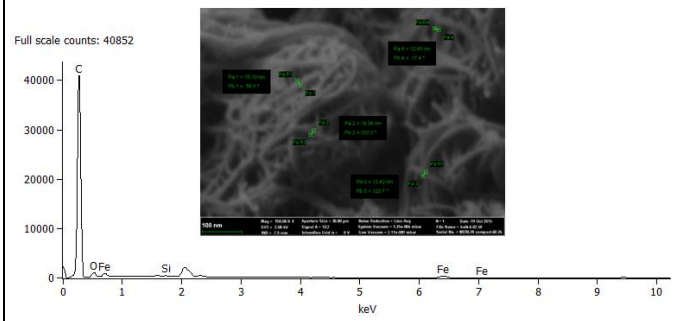
(b)

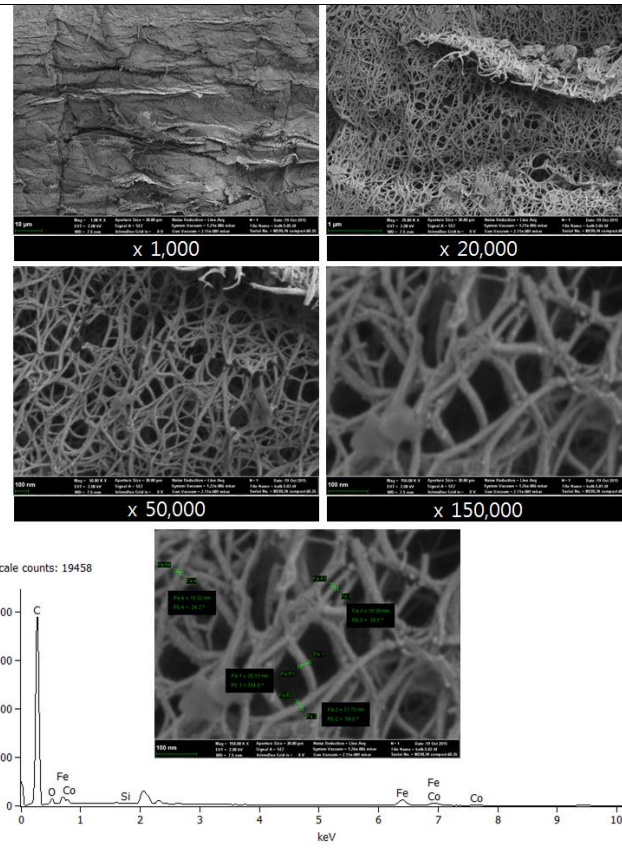
Appendix 3. The SEM images of tested materials in this study

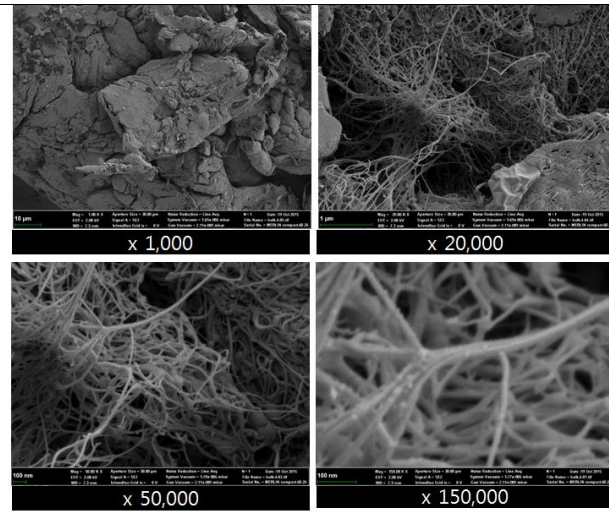
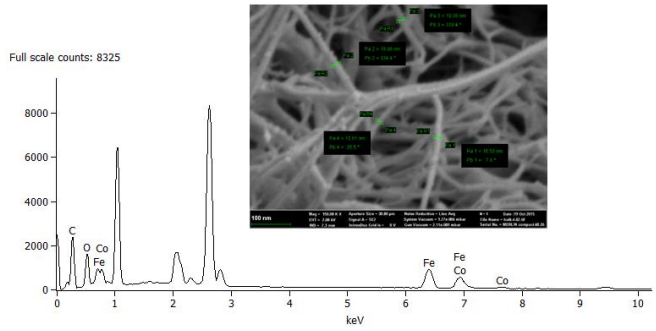
Supplier	Types	SEM images
Carbon nanotech	MWCNT 1	  * Detected elements by SEM/EDX: C, Fe, Al, Mg, Si

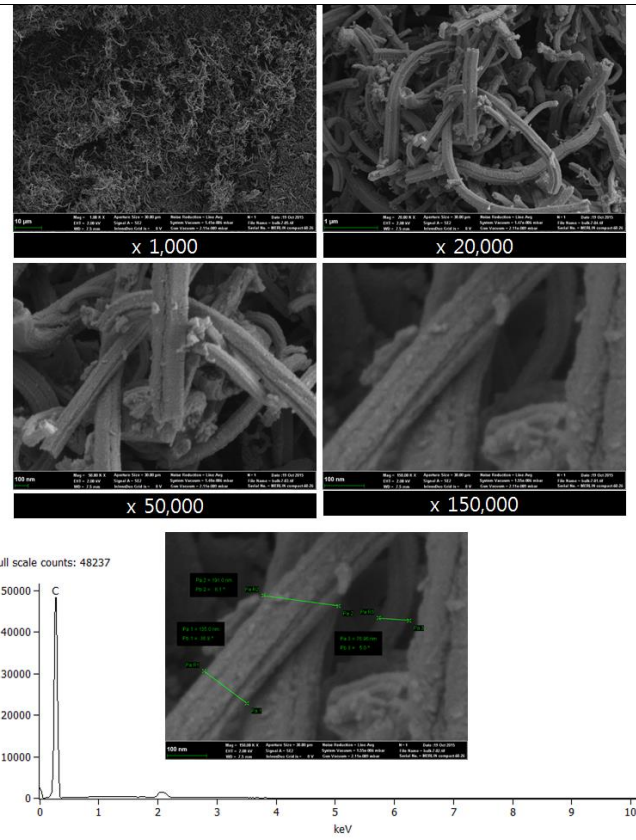
Hyosung	MWCNT 2	 * Detected elements by SEM/EDX: C, Fe, Al, Mg, Si

Hanwha chemical	MWCNT 3	  * Detected elements by SEM/EDX: C, Fe, Al, Si, Mo

Kumho chemical	SWCNT 1	  * Detected elements by SEM/EDX: C, Fe, Si

Kumho chemical	SWCNT 2	 * Detected elements by SEM/EDX: C, Fe, Co, Si

Carbon nanotech	SWCNT - 3	  * Detected elements by SEM/EDX: C, Fe, Co, Si

Carbon nanotech	CNF	 * Detected elements by SEM/EDX: C

Appendix 4. Thermograms for SWCNT (upper), CNF (middle), and MWCNT (lower).