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A Proposal of Method for Evaluating Airborne MWCNT Concentration

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Abstract: As multi-wall carbon nanotubes (MWCNTs) come to be used in a wider range of products, increasing production is expected to result in greater exposure of workers to MWCNTs. In this research, we present a method for evaluating the concentration of MWCNT aerosols distinctively on the basis of the elemental carbon (EC) concentration. Respirable dust is sampled using a Sioutas cascade impactor (SCI) for a certain volume of workplace air. The SCI can collect size-segregated particles having aerodynamic diameters of 2.5 μm, 1.0 μm, 0.5 μm, 0.25 μm and <0.25 μm. MWCNTs in sampled particles are determined by carbon analysis. Based on the phenomenon that MWCNTs easily aggregate/agglomerate, the present procedure for distinguishing MWCNTs uses the EC in particles larger than 1 μm as an index of MWCNT; the EC is oxidized at a high temperature, 920°C, in carbon analysis. We propose a three-step procedure for distinguishing between MWCNT aerosol and atmospheric particulate matter, and for measuring MWCNT concentrations in workplace air on the basis of EC concentration.

Key words: MWCNT, Nanotube, Exposure assessment, Sioutas cascade impactor, Elemental carbon, Carbon analysis

Introduction

Recently, powders having a size of several tens of nanometers have been widely used because they attain electrical, physical and chemical characteristics different from those of the bulk material, even though they have the same chemical composition. Such powders are called nanomaterials. Materials containing nanomaterials and having at least one dimension less than 100 nm with their original shape and/or aggregates/agglomerates are also called nanomaterials. Probable health effects related to the characteristics of nanomaterials have been proposed, and the health effects are of concern in work environments where workers are probably exposed to nanomaterials. Measuring methods for the concentration of the nanomaterials are needed for the work environment evaluation and exposure assessment[1–4].

Since chemical vapor deposition process for carbon nanotube (CNT) production was developed in Japan[5], CNT production rate has increased. The multi-wall CNT (MWCNT) is one of carbonaceous nanomaterials and has various shapes such as straight tubes, curved tubes, and so on. MWCNTs are considered to affect pulmonary function via inhalation route. All MWCNTs are not categorized as fibers by the WHO's criteria[6] because MWCNTs are often observed as aggregates/agglomerates. A practical method of monitoring MWCNT in work environments involves measurement of carbon[7–10].

At present, no concentration level, such as a permissible exposure level (PEL) for MWCNT, has been set by any governments to date. The probable PEL values for workplace MWCNTs are being discussed. These values being discussed have been derived from hazard assessment data from inhalation studies conducted by a few

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groups[11–13]. In-house PELs or preliminary estimated levels have been proposed[13–15]. Even though a PEL has not been set, it is worth discussing suitable measurement methods for low concentration of MWCNT aerosols in workplaces.

For CNTs, it is difficult to find a sensitive and selective analytical method because the main component of CNTs is carbon. It is necessary to distinguish between carbon originating from CNTs and that from combustion sources. In this research, we propose a method for evaluating airborne MWCNT concentration using elemental carbon (EC) and for distinguishing airborne MWCNTs from other background particulate matter (PM) such as diesel exhaust particles (DEPs) that can interfere with the measurement. In our proposed method, at first, size-segregated particles are collected using an impactor, and EC concentration of the collected particles is measured by carbon analysis. Then, the MWCNT presence is evaluated using our proposed procedure, and determined. We assessed the effectiveness of this method in measuring 1 to 100 μg/m^3 of MWCNT in a work environment and for distinguishing MWCNTs from ambient PM.

Method

Airborne particles were collected using a Sioutas cascade impactor (SCI; SKC Inc., Eighty Four, PA, USA)[16], and EC in the particles was analyzed using a carbon monitor. After MWCNT-origin EC was distinguished from other EC from ambient PM by the procedure proposed in this research, airborne MWCNT concentration was quantified using the EC oxidized at a high temperature. A schematic of this procedure is shown in Fig. 1.

The SCI is designed to collect size-segregated particles with five stages of 2.5 μm, 1.0 μm, 0.5 μm, 0.25 μm and smaller than 0.25 μm at a flow rate of 9 l/min. The upper four stages are called stages A to D, and the final stage is a back-up filter. A quartz fiber filter (2500QAT-UP, PALL, Port Washington, NY, USA) is used to collect particles. The filter is pre-heat-treated at 550°C for 4 h before sampling. Particles are collected in a line 20 mm length on stages A to D using the SCI which is a slit-type impactor. The SCI is suitable for carbon analysis because particles are collected in a line and concentrated. Carbon analysis can only be conducted by cutting out 1.5 × 1 cm or 1 × 1 cm samples from the filter of each stage without any pre-treatment such as solvent extraction.

Generation and sampling of simulated aerosol of MWCNTs using SCI

In order to observe the manner in which fibrous MWCNTs are collected by SCI, simulated MWCNT aerosol generated by a fluidized bed[17] was sampled on a quartz fiber filter using the SCI. Reagent MWCNT (reagent No. 659258, diameter 110 nm, length 5–9 μm, carbon contents >90%, Sigma-Aldrich, St. Louis, MO, USA) was fluidized with glass beads in a 500-ml glass

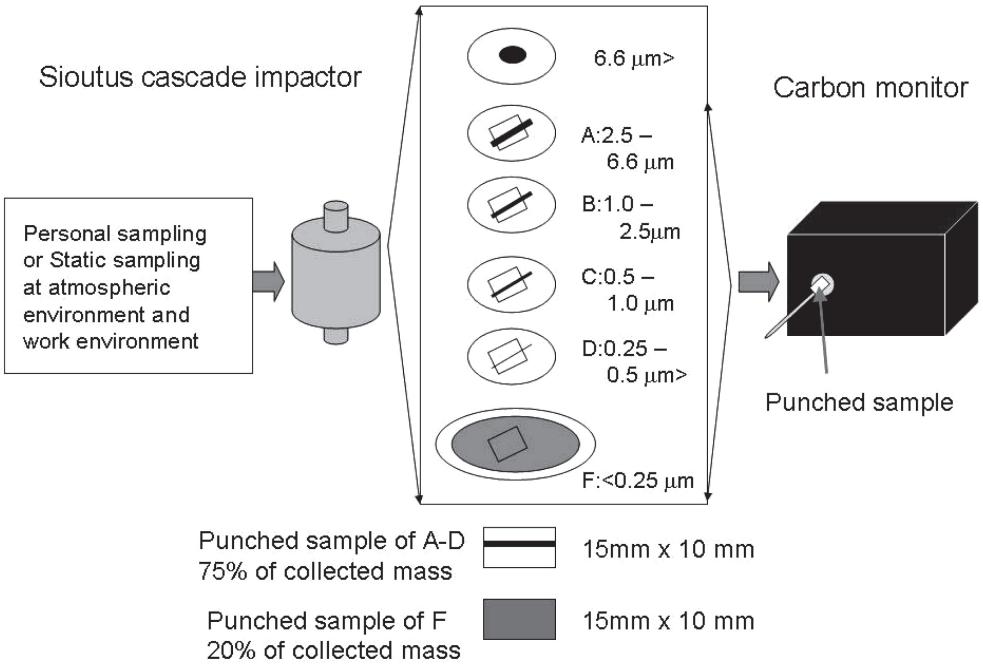


Fig. 1. Schematic diagram of sampling and analysis of ambient MWCNT particles.

bottle set on a shaker. We used this reagent MWCNT as a simulant of airborne MWCNTs in a work environment.

An additional collection stage was added above stage A to eliminate coarse particles, although this is not the ordinary usage of the SCI. The size of the 50% cut-point of the additional stage is 6.6 μm as calculated from the diameter of the SCI inlet when the flow rate is 9 l/min. The cut size is larger than 4 μm; however, this stage eliminates coarse particles not related to the inhalation of respirable particles.

Mass measurement of MWCNT was performed with a mass balance, Sartorius CP2P-F (Sartorius AG, Goettingen, Germany), having a minimum sensitivity of 1 μg.

For scanning electron microscopic (SEM) observation, simulated MWCNT aerosol was collected on a silver membrane filter (pore size: 5 μm; Sterlitech Corporation, Kent, WA, U.S.A.) to avoid interference from fibers of quartz fiber filter. A field emission type SEM (Hitachi S-4700, Tokyo) was used to observe MWCNT.

Sampling of aerosols at workplaces with/without handling MWCNTs using SCI

Eight samples were collected by SCI and analyzed. The samples were obtained at the following sampling sites: two samples were obtained during maintenance work of instruments used for heat treatment of MWCNTs; two samples were obtained at a site where manual packing of MWCNTs was conducted during and not during the packing operation; two samples at a site where automated packing was conducted with enclosure during and not during the operation; and one sample was obtained outside of the factory at 5 m from the air inlet to the factory; one ambient air sample was obtained at a different place and occasion from the above samples near a heavy-traffic road in a large city[20].

Sampling sites in workplaces were selected because they had been recognized as emission sources of MWCNT through preliminary assessment. Samples were collected with the SCI using stationary sampling near the place of the manual packing operation and near the instrument used for automated packing operation. The sampling height was 1–1.5 m, the sampling duration in the workplace was 1–3 h depending on the work shift, and for ambient air it was 7.5 h at the longest.

Analysis of samples collected using the SCI

A detailed description of the punched sample is shown in Table 1. For usual analytical procedure, a punched sample X (1.5 × 1 cm) was analyzed. To observe the collection behavior of the SCI for MWCNT, the left part L was also analyzed by cutting the filter into pieces to put on a quartz spoon, which was used in a carbon monitor. The analyzed amount of EC on one stage is the sum of that on both X and L, that is, EC(Stage) = EC(X) + EC(L). For stages A to D, the calculated amount of EC(Stage) is EC(X)/0.75. For the back-up filter, the whole filter area and punched area are 8.0 cm^2 and 1.5 cm^2, respectively, EC(Stage) is calculated as EC(X)/0.19 on the basis that the particles are collected uniformly by filtration sampling.

Carbon monitor

It is well known that DEPs contain a large amount of EC. Some instruments are designed for measuring the carbon content in particles obtained from workplace air and the general environment to assess the contribution of DEPs in an environment[18, 19]. In carbon analysis using such instruments, a quartz fiber filter sample is thermally treated in helium atmosphere, then oxygen is added to the atmosphere to evolve or oxidize the carbon

Table 1. Sample shape and estimated amount of component on each sample

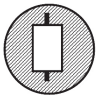
Name of sample	Stage	X	L
	Length of line: 2 cm 	Length of line: 1.5 cm 	
Ratios of line length, when Stage is 1	1	0.75	0.25
	Area: 8.0 cm^2 	Area: 1.5 cm^2 	
Ratios of filter area, when Stage is 1	1	0.19	

Table 2. Protocol for MWCNT analysis by carbon monitor

	Temperature (°C)	Duration (sec)	Gas
OC1	120	180	He
OC2	250	180	He
OC3	450	180	He
OC4	550	180	He
EC1	550	240	2% O_2/He
EC2	700	360	2% O_2/He
EC3	920	600	2% O_2/He

component. Evolved carbon is oxidized to carbon dioxide by catalysis, and is reduced into methane by catalysis to determine carbon amount using a flame ionized detector. During carbon analysis, organic carbon (OC) and EC amounts are mainly determined without oxygen and with oxygen, respectively.

In the present study, a thermal/optical carbon monitor (Sunset Laboratory Inc., Tigard, OR, USA) was used. The protocol, a program for controlling the temperature and atmospheric gas of the instrument, used in this study was slightly modified IMPROVE protocol (Table 2)[19]. We used a final temperature of 920°C in the protocol to oxidize MWCNT quantitatively, because some MWCNT were not oxidized at 850°C, the usual temperature of the final stage of the protocol, in our preliminary experiments. In the IMPROVE protocol, EC is categorized into EC1, EC2 and EC3 according to the oxidized temperature. MWCNTs are usually observed as EC3, and some MWCNTs thinner than 10 nm are mainly observed as EC2. The measurable range of EC3 on a punched filter for one analysis is 0.5–50 μg.

Results

Collection of simulated aerosol of MWCNT and recovery

Simulated aerosol of MWCNT was sampled using the SCI as shown in Fig. 1. Figure 2 shows SEM images of MWCNT 659258 collected on silver membrane filters. Agglomerates having aerodynamic diameters >2.5 μm and 1.0–2.5 μm, were observed on stages A and B. MWCNT 659258 was well dispersed and single

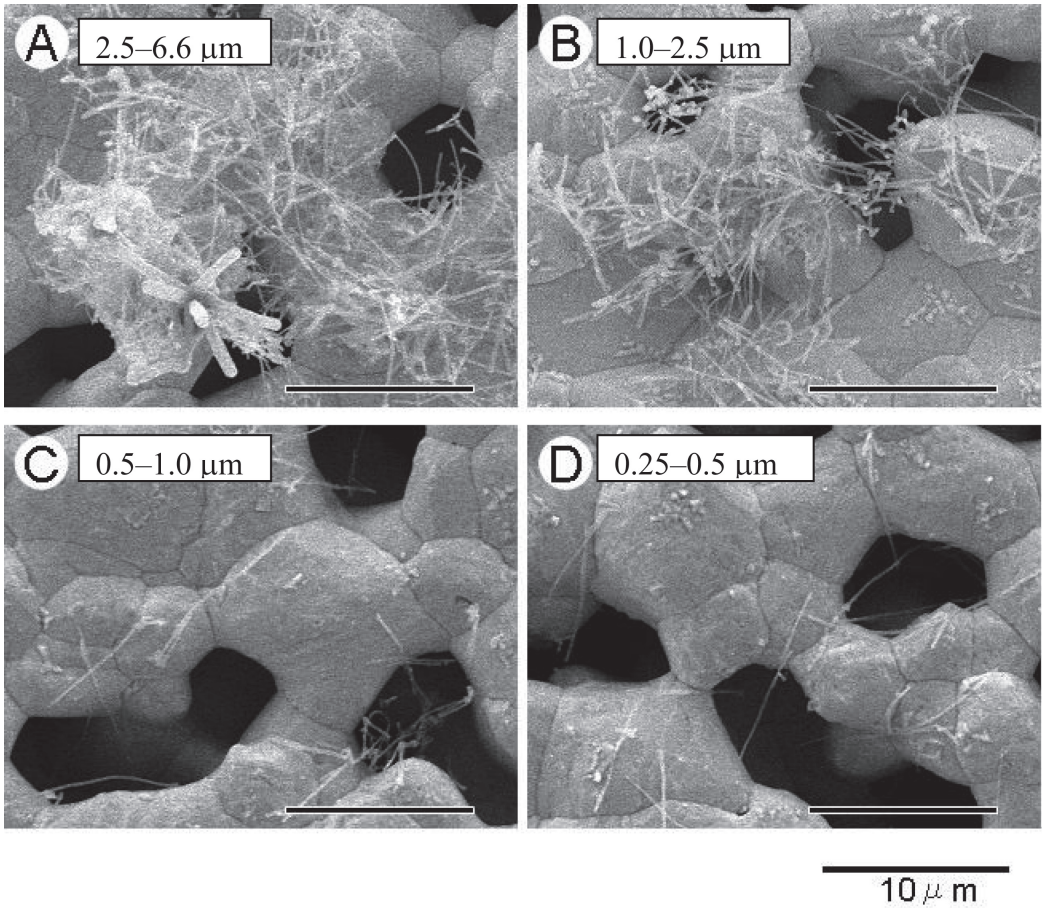


Fig. 2. SEM images of simulated MWCNT aerosols collected on stages A, B, C and D of SCI.
A: >2.5 μm, B: 1.0–2.5 μm, C: 0.50–1.0 μm, D: 0.25–0.50 μm.

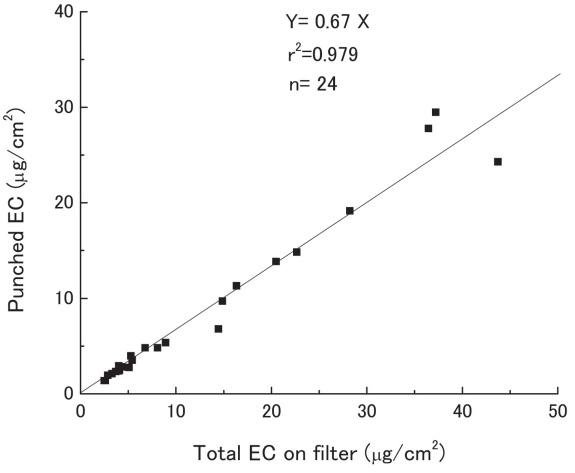


Fig. 3. Ratio of EC on punched area versus whole filter of stages A to D for simulated MWCNT aerosol.

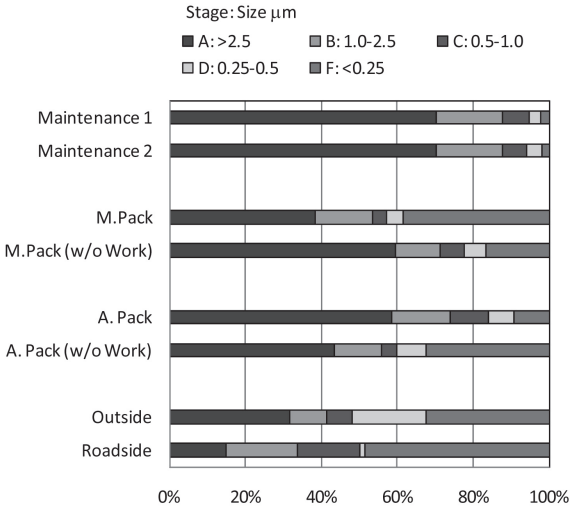


Fig. 4. Proportions of EC3 in different sizes of particles collected from various environments.
A.Pack: Automated packing, M.Pack: Manual packing.

fibers were observed on stages C and D (0.5–1.0 μm, 0.25–0.5 μm). Particles collected in the workplace had similar appearances according to the SEM observations: agglomerates on stages A and B, and smaller agglomerates and fibers on stages C and D.

For stages from A to D, the punched sample and the left part of the same sample (Table 1) were analyzed. As shown in Fig. 3, EC for the punched sample (EC(X)) and EC for a whole filter at each stage (EC(X) + EC(L)) showed a good correlation (correlation coefficient: 0.98). The slope of this line was estimated to be the same as the ratio of the punched length to the slit nozzle size, 0.75 (1.5 cm/2 cm). As the experimental result was 0.67, the error of analysis of the punched sample was around 10%. EC3 was 4 to 11 times higher than EC2, and almost all of the simulant MWCNTs were observed as EC3.

Aerosols from workplace and ambient air

In the present study, we determine the environment MWCNT on the basis of EC3, because only EC3 was detected for MWCNTs sampled at the workplace. However, to evaluate the MWCNT concentration on the safe side, the sum of EC2 and EC3 should be used, when some MWCNT is observed as EC2 and EC3.

Size distribution of EC3

Figure 4 shows the proportion of EC3 on each stage of the SCI for the particles collected in various environments. In workplaces, agglomerated MWCNTs were dominant. During maintenance of instruments, when the highest concentration was observed, 80% of EC3 was observed in stages A and B, that is, in particles larger than 1 μm. With or without work in the manual packing operation, the proportion of EC3 in particles larger than 1 μm was larger than 50%. For automated packing process, the same tendency was observed for with or without process: the proportion of EC3 in particles larger than 1 μm was larger than 50%.

To compare the data of background particles, data for outside the factory and for the heavy-traffic roadside[20] are also shown in Fig. 4. The EC3 proportion was high for particles <0.25 μm. For these samples, 40% of total EC3 was observed in stages A and B. Therefore, if the size fraction of EC3 exceeds 50% in the size range greater than 1 μm, it can be considered as an indication of the presence of MWCNTs in the investigated atmosphere.

EC3 to EC2 ratios

EC1 and EC2 are dominant in ambient fine PM, but EC3 is scarce. The MWCNT aerosol monitored in this research shows that, among EC1 to EC3, EC3 shows the largest amount. EC2 and EC3 indicate the presence of graphitic carbon and are considered to be the index of EC from incomplete combustion[21]. Therefore, we considered that the ratio of EC3 to EC2 is an index of MWCNT's contribution to the sample particles. Figure 5 shows EC3/EC2 for the sampled particles at the same sites as shown in Fig. 4. For every environment during work, for example, maintenance and manual/automated packing, EC3 was larger than EC2 and the ratio was greater than 3 for stages A to B. Even without work, EC3 was present in a large amount in larger particles in the manual packing environment. For particles smaller than 0.5 μm, the ratio EC3/EC2 was much lower than that for larger particles. From these results and SEM observations of collected aerosols, when EC3

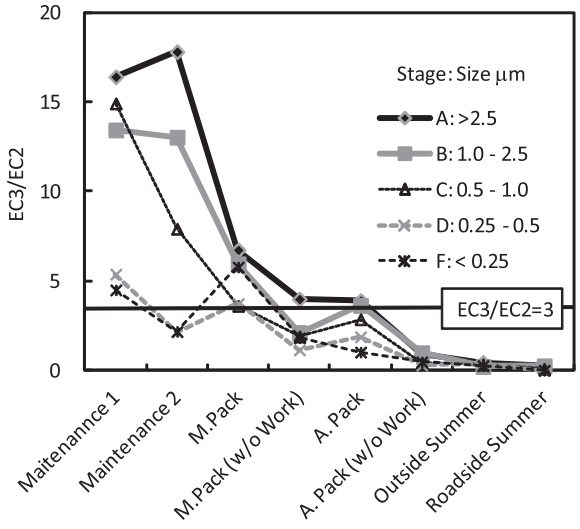


Fig. 5. EC3/EC2 ratios in different size of particles collected from various environments.
A.Pack: Automated packing, M.Pack: Manual packing.

to EC2 ratio is greater than 3 for particles larger than 1 μm, the ratio is considered as an indication of the presence of MWCNT.

Discussion

What concentration of MWCNT can be measured by this method?

For measurements using a carbon monitor, the limit of quantitation is around 1 μg. This means stages A to D need more than 1.5 μg EC3 on each stage because 67% of EC3 is analyzed in one punch from the filter (Table 1). If only one stage between A and D collects all particles and the sample volume is 1 m^3, the quantitation limit is expected to be 1.5 $\mu g/m^3$. For the back-up filter, the quantitation limit is expect to be 5.3 $\mu g/m^3$. As the flow rate of SCI is 9 l/min, sampling of 1 m^3 takes 111 min. If sampling extended to 8 h, sampling volume is 4.32 m^3, and the quantitation limit becomes lower.

In the present study, background concentration of EC3 was also measured outside the facility, and the EC3 concentration was lower than 1 $\mu g/m^3$ (4 m^3-sampling). At heavy traffic roadside, which is the same site shown in Fig. 4, EC3 was around 1 $\mu g/m^3$ (52 m^3-sampling). If high concentration is expected for background, the limit of detection becomes higher. Background concentration should be measured outside facility or at some place inside facility representing background environment.

Interpretation of results and the proposal for a measurement method of MWCNTs agglomerates and single fibers

The SCI is designed to separately collect particles such as respirable, $PM_{2.5}$, PM1, and ultrafine particles. In a workplace where MWCNTs are handled, MWCNTs are observed as particles of various sizes. When EC3 is observed in respirable dust (stage A) and $PM_{2.5}$ (stage B), MWCNTs are expected to exist as agglomerates as shown in Fig. 2, and the contribution of background particles like DEPs is small. On stage C, agglomerates and single fibers are expected to coexist, and the degree of agglomeration can be dependent on the shape of the MWCNTs. When EC is observed on stage D and the back-up filter, both dispersed MWCNTs and DEPs are expected to coexist. SEM observation of sampled particles would help to clarify what types of particles are actually present.

An in-house PEL, for example, proposed by Bayer[14], has been used for both agglomerates and single fibers. However, in the light of recent research into hazard assessment of agglomerated MWCNTs and single fibers, a method for separately measuring agglomerates and single fibers may be necessary.

For work environment evaluation, not all stages of the SCI may be necessary, but 50% cut-off diameters of 4 μm and 1 μm are necessary for assessing respirable dust and to judge the presence of less agglomerated MWCNTs, respectively.

Distinguishing between MWCNTs and background particles using a carbon monitor

A flowchart for determining the presence of MWCNTs is shown in Fig. 6. The judgment procedure by assessing EC value is as follows.

Step 1: The difference between EC2+EC3 concentrations inside and outside of the workplace is determined. This step can roughly check the presence of MWCNT, even if some MWCNT is not detected as EC3.

Step 2: The proportion of EC3 on stages A and B relative to total particles collected on all stages of the SCI is determined.

Step 3: The ratio of EC3 on stages A and B to EC2 on stages A and B is determined.

The latter two steps are based on the observation that EC in particles with an aerodynamic diameter larger than 1 μm, which is oxidized mainly at higher temperatures, consisting of agglomerates of MWCNTs.

Judgment results regarding the presence or absence of MWCNTs according to the flowchart shown in Fig. 6 are shown in Table 3. In this table, 'Yes' means MWCNT is judged to be present. In Step 1, inside concentrations are higher than outside in most work

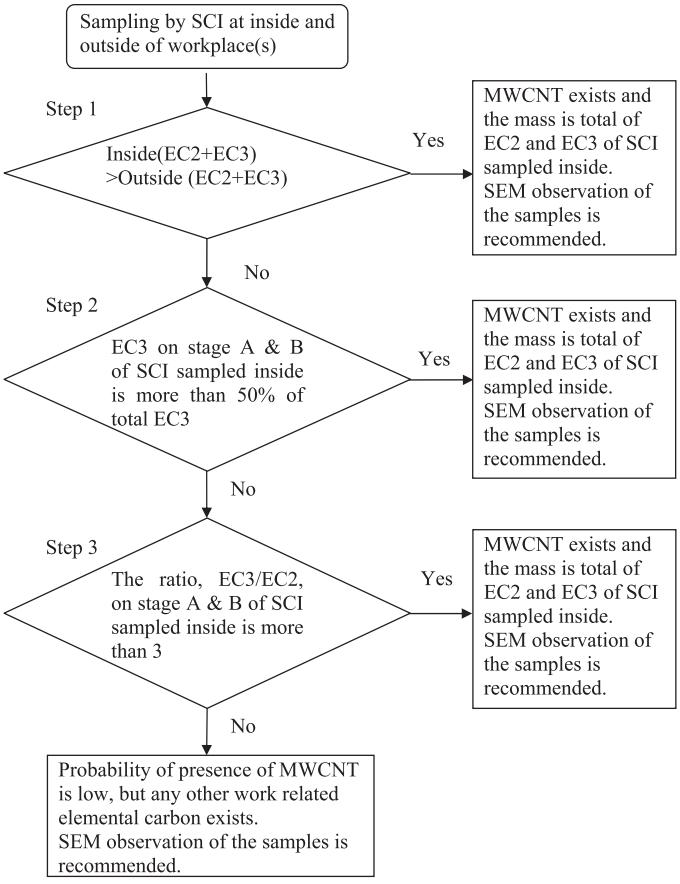


Fig. 6. A flowchart for distinguishing MWCNT from background carbonaceous particles.

Table 3. Judgments of presence of MWCNT for particles sampled in various work environments

	Step1		Step 2		Step 3	
	Inside > Outside		> 50%		> 3	
	EC2 + EC3 Inside/Outside	MW CNT	EC3 (A + B) /EC3 (Total)	MW CNT	EC3 (A + B) /EC2 (A + B)	MW CNT
Maintenance 1	127.9	Yes	87.8%	Yes	15.7	Yes
Maintenance 2	67.7	Yes	87.7%	Yes	16.6	Yes
Manual packing	21.5	Yes	53.5%	Yes	6.5	Yes
Manual packing w/o Work	4.2	Yes	71.2%	Yes	3.5	Yes
Automated packing	9.9	Yes	74.1%	Yes	3.9	Yes
Automated packing w/o Work Enclosed	1.0	No	55.9%	Yes	0.9	No
Outside	1.0	No	41.4%	No	0.4	No

environments, which showed reasonable judgment. For the judgment criterion of Step 2, when work-related MWCNTs are determined to be present, EC3(A+B) as a percentage of EC3(Total) should be more than 50%. In judgment Step 3, the value should be more than 3. In environments with higher probabilities of MWCNT presence, such as maintenance and manual packing, EC3(A+B)/EC2(A+B) are greater than 3 and it is judged that MWCNTs are present. This judgment is supported by SEM observation. The efficacy of this procedure needs to be confirmed in other workplaces and for various types of MWCNTs.

The concentration of MWCNTs is evaluated using the sum of the amounts of EC2 and EC3 after confirmed

by the judgment based on the flowchart given in Fig. 6 and SEM observation.

Is this procedure applicable to other carbonaceous nanomaterials?

SWCNTs (single-wall CNTs) usually start oxidation at EC1 and oxidation finish at EC2. MWCNTs thinner than 10 nm are analyzed as EC2. In such cases, the judgment will not always be 'Yes'. However, when analysis indicates the existence of work-related EC, SEM observation is necessary.

Carbon black and thick fibers like graphite fibers are mainly oxidized at EC3. Thick fibers are sometimes not oxidized, even at 920°C. Samples left after carbon analysis can be oxidized by adding a transition metal, for example, iron solution, then the presence of residual EC can be confirmed. Our proposed procedure is applicable to detection/measurement of these materials, but care should be taken with MWCNT measurement when other carbonaceous materials are present in the same environment because of positive interference from them.

To conclude, even in environments where background particles are present, the EC oxidized at high temperature in aerodynamically micron-size particles can be an index of MWCNTs after determining whether MWCNTs are present using the procedure proposed in this study.

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