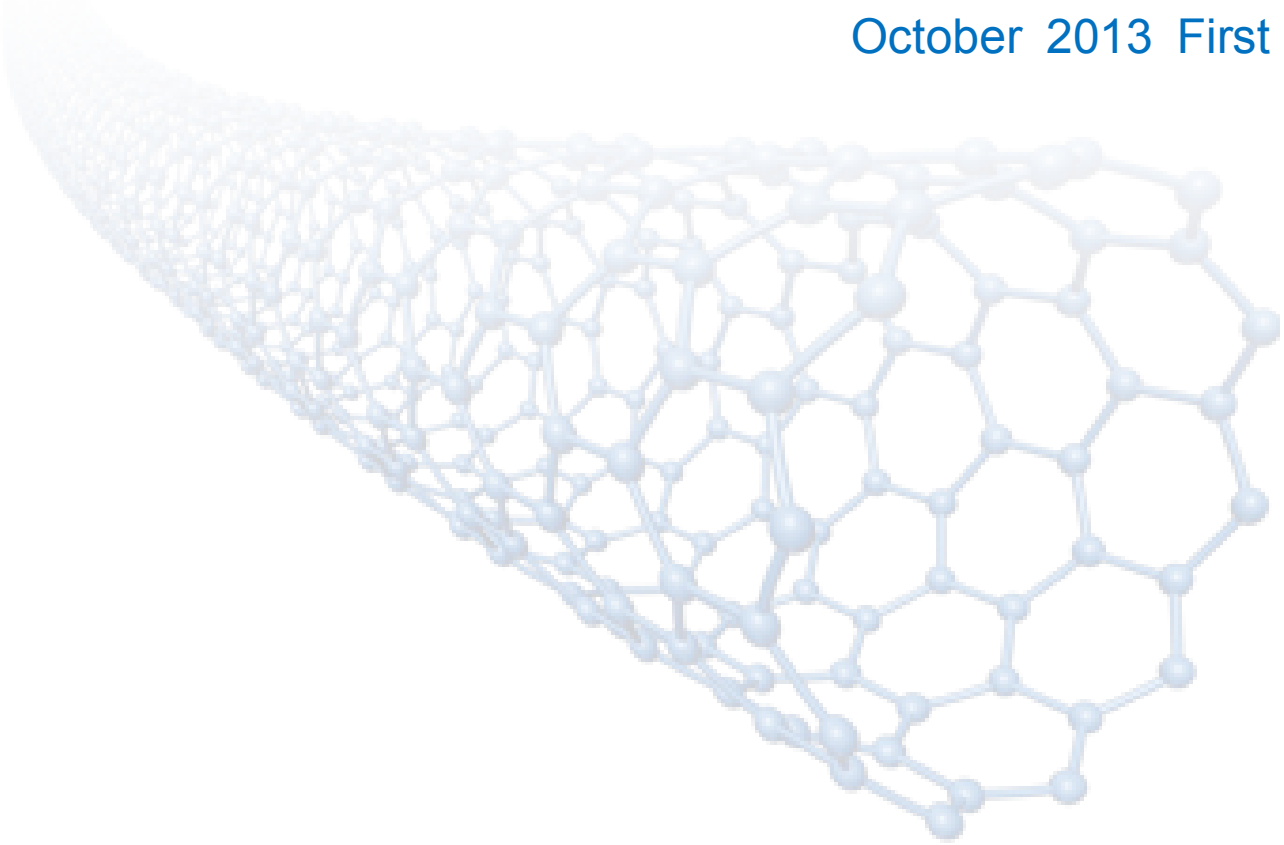
Guide to measuring airborne carbon nanotubes in workplaces

October 2013 First edition



Technology Research Association for Single Wall Carbon Nanotubes (TASC)

Research Institute of Science for Safety and Sustainability (RISS),
National Institute of Advanced Industrial Science and Technology (AIST)

Guide to measuring airborne carbon nanotubes in workplaces

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This document and other related documents (e.g., Protocols of preparation, characterization and in vitro cell based assays for safety testing of carbon nanotubes) produced by TASC and AIST-RISS can be downloaded from the AIST-RISS website. http://www.aist-riss.jp/main/modules/product/nano_tasc.html

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About this guide

Carbon nanotubes (CNTs) have unique properties (e.g., ultra-light weight, super strength, great flexibility, and high electrical and thermal conductivities) that make them potentially useful in many applications. The Technology Research Association for Single Wall Carbon Nanotubes (TASC)—a consortium of nine companies and the National Institute of Advanced Industrial Science and Technology (AIST)—was founded on May 24, 2010, and is engaged in research and development on single-wall CNTs (SWCNTs) in order to establish a new industry on their composite materials under the project "Innovative carbon nanotubes composite materials project toward achieving a low-carbon society" (no. P10024), which is sponsored by the New Energy and Industrial Technology Development Organization (NEDO). As part of the project, under the initiative of Research Institute of Science for Safety and Sustainability (RISS), a research unit of the AIST, we are developing methods for ensuring safety of CNTs.

Occupational exposure limits (OELs) for CNTs have been proposed recently (see Section 1.2). Appropriate exposure controls and measurement methods are required for working environments where CNTs are handled. To this end, we are developing and evaluating methods for measuring airborne CNTs.

As a direct result of the project, we publish this document, which is a guide to measuring airborne CNTs in workplaces, as a means of CNT safety management. This guide summarizes the available practical methods for measuring airborne CNTs and presents measurement cases performed by TASC. A specific method is yet to be definitively determined, and many challenges still remain. Nevertheless, we hope this guide is helpful with regard to voluntary safety management of CNTs. We will be grateful if you share with us your comments, opinions, and requests regarding the contents of this guide.

October, 2013

Executive summary

Section 1 discusses current status of working environment measurement for carbon nanotubes (CNTs) and other nanomaterials. Currently, the measurement of airborne nanomaterials is performed primarily with real-time aerosol measuring instruments and through gravimetric analysis, chemical analysis, and electron microscope observation of particles collected with filters and others.

Although there is no legally enforceable occupational exposure limit (OEL) for CNTs, recommended OELs have been suggested by several organizations and companies (~1–50 μg/m^3, Table 1.1 in Section 1.2). These OELs are determined as values of mass concentration and are often proposed for values of a respirable particle concentration (values that exclude coarse particles that do not reach the lungs; by the ISO7708 definition, 4-μm particles are reduced by 50%).

The appropriate metric for assessing health effects is yet to be definitively determined, and many challenges still remain (e.g., discrimination between CNTs and background particles, measurement of CNTs released from composite materials, and developing simple and inexpensive measuring methods)

Section 2 summarizes available (relatively simple) methods for measuring airborne CNTs: on-line (portable) aerosol measurement (e.g., black carbon monitor; see Table 2.1 in Section 2.1), off-line quantitative analysis (e.g., thermal carbon analysis; see Table 2.2 in Section 2.2), and particle sampling methods for electron microscope observation (see Table 2.3 in Section 2.3). The advantages, disadvantages, and usefulness of each of the measuring methods are summarized in Table E1. In addition, application examples for individual measurement methods are given in Fig. E1 with respect to the purpose of measuring airborne CNTs.

With the object of safety management of CNTs, a major concern is a comparison with the OEL in most cases; therefore, (3) and (5) in Fig. E1 can be considered important. An example of practical methods for measuring airborne CNTs with the object of safety management of CNTs is given in Fig. E2. For accurate quantitative determination of CNTs and comparison with the OEL, thermal carbon analysis is effective in many cases. However, this method is not necessarily suitable for daily exposure control because they require filter collection of particles, typically for a few hours, and the instruments are relatively expensive. For daily exposure control, portable aerosol measuring instruments (e.g., black carbon monitor: BCM) are preferable. These instruments have the ability to obtain real-time results in situ. An appropriate combination of an accurate detailed method and a simple real-time method is a reasonable way for continued management of CNT exposure.

Table E1 Advantages, disadvantages, and usefulness of individual measurement methods (=Table 2.4)

	Advantage	Disadvantage	Usefulness
On-line (portable) aerosol measurement	Easy, inexpensive, time response, real time	Discriminating from particles other than CNTs	Grasp of spatial–temporal distribution, daily monitoring
Off-line quantitative analysis	Quantitative determination (by mass), CNT identification	Sampling over long periods, expensive equipment	Comparison with OEL
Electron microscope observation	CNT identification, morphology observation	Particle collection, observation cost (effort, time)	Verifying existence of CNTs, understanding the shape

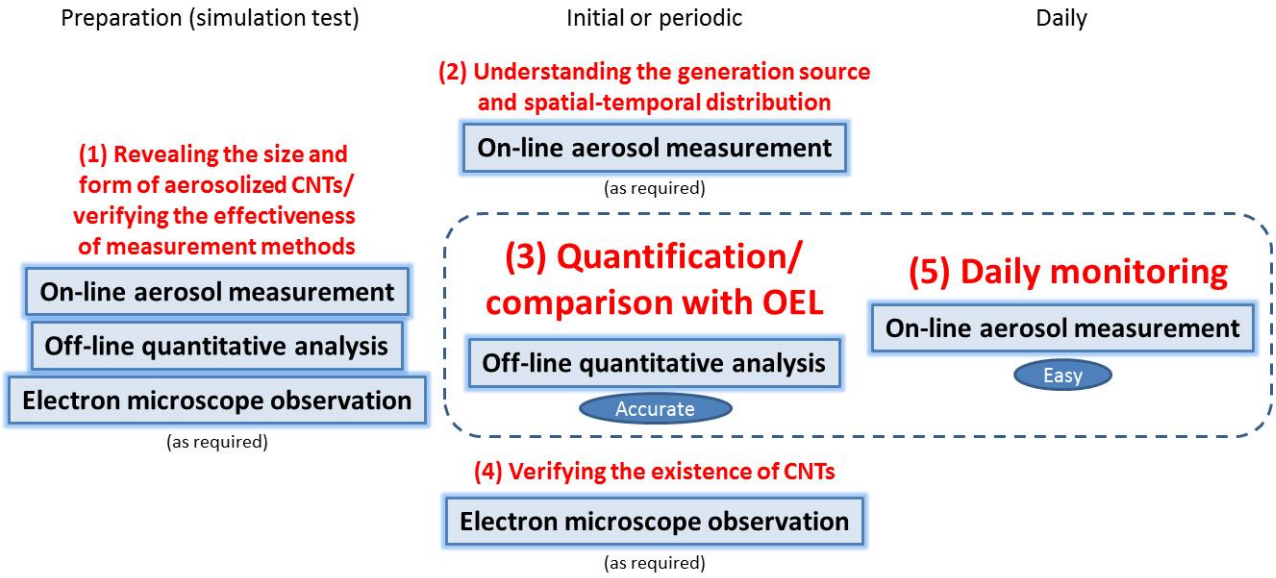

Figure E1 Application examples of individual measurement methods according to the purpose of measuring airborne CNTs. (=Figure 2.4)

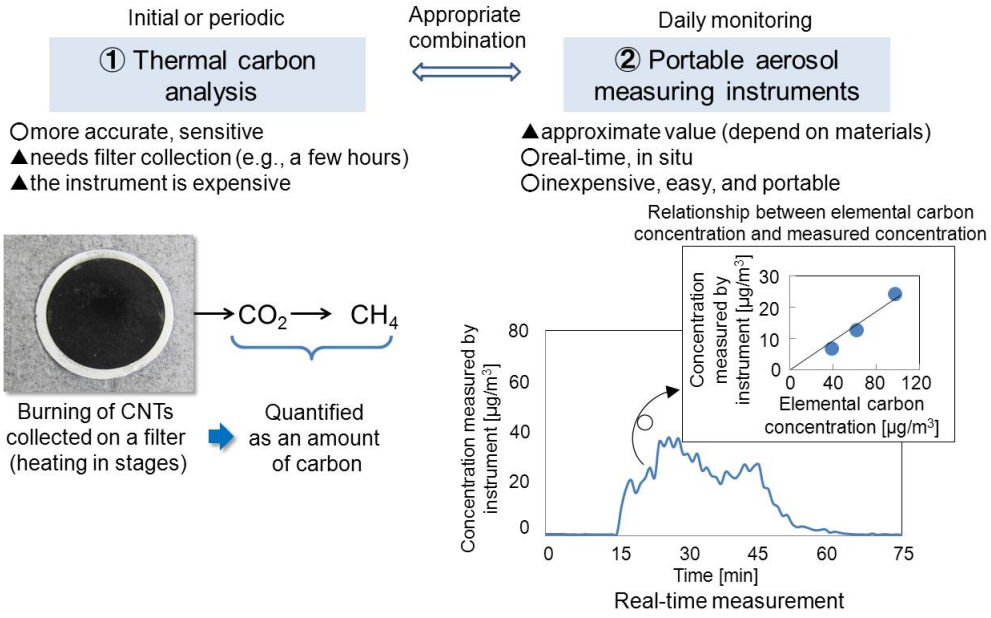

Figure E2 An example of practical methods for measuring airborne CNTs with the object of safety management of CNTs. (=Figure 2.5)

Section 3 presents the measurement cases that were performed by TASC.

Section 3.1 provides an evaluation of CNT quantification by thermal carbon analysis. The elemental carbon (EC) mass of approximately 100 μg of CNT powder placed in an Au (or Pt) foil boat was measured by thermal carbon analysis and compared with the mass of CNT powder gravimetrically measured by an ultra-microbalance. The obtained ratios of the EC mass to the overall CNT mass were consistent with or slightly lower than the carbon purity reported by the manufacturers and others. These results were reasonable because the carbon purity obtained through thermal carbon analysis was the EC content per unit mass of non-pretreated CNT powder, which likely contains adsorbed water and volatile gas. Thus, thermal carbon analysis is considered capable of quantifying CNTs.

Section 3.2 provides a measurement example of the particle size distribution and form of CNTs. CNTs were aerosolized by vortex shaking. The particle size distributions measured by aerosol measuring instruments spanned a broad range, from nano to micron size. In electron microscopic observations, many of the collected CNTs were submicron- and micron-sized agglomerated particles. The CNTs appear different according to their type and tube diameter. Single-wall CNTs with a fine tube diameter showed a net-like or flock-like form, and multiwall CNTs with a narrow tube diameter showed a wool-like form. On the other hand, multiwall CNTs with thick tube diameter showed a rod-like form.

Section 3.3 gives a method for evaluating the response of a BCM and a photometer to airborne CNTs. These instruments exhibited linear responses to CNT mass concentrations. However, their responses tended to depends on particle size and decrease with increasing agglomeration sizes of airborne CNTs. Furthermore, the BCM sensitivity gradually decreased with increasing filter load even before the instrument status indicates overloading. The reason might be attributed to the clean environmental conditions (i.e., the absence of interfering light-scattering materials).

Section 3.4 gives a case of the measurement of airborne CNTs in the presence of background aerosols using portable aerosol measuring instruments. The measurements were conducted when simulating handling CNTs. Since CNTs agglomerated easily, a concentration increase was seen with particles from the submicron to micron size. On the other hand, no increase in concentration was observed with nano-sized particles since the background concentration for nano-sized particles was relatively high. The optical particle counter and the BCM were effective for measuring airborne CNTs in terms of discrimination from background particles.

Section 3.5 gives a case of the measurement performed in a pilot-scale plant where CNTs are synthesized, harvested, and packed. CNTs released in the enclosure during the harvesting and packing could be identified through thermal carbon analysis and electron microscope observations.

Contents

Abbreviations

AIST	National Institute of Advanced Industrial Science and Technology
APS	aerodynamic particle sizer
BCM	black carbon monitor
CNF	carbon nanofiber
CNT	carbon nanotube
CPC	condensation particle counter
EC	elemental carbon
EDX	energy dispersive x-ray spectroscopy
ELPI	electrical low pressure impactor
FE-SEM	field emission scanning electron microscope
FMPS	fast mobility particle sizer
HEPA	high efficiency particulate air (filter)
ICP-AES	inductively coupled plasma - atomic emission spectrometry
ICP-MS	inductively coupled plasma - mass spectrometry
ISO	International Standard organization
JNIOSH	National Institute of Occupational Safety and Health, Japan
MWCNT	multiwall carbon nanotube
NEDO	New Energy and Industrial Technology Development Organization
NIOSH	National Institute for Occupational Safety and Health
OC	organic carbon
OECD	Organisation for Economic Co-operation and Development
OEL	occupational exposure limit
OPC	optical particle counter
REL	recommended exposure limit
RISS	Research Institute of Science for Safety and Sustainability
SEM	scanning electron microscope
SMPS	scanning mobility particle sizer
SWCNT	single-wall carbon nanotube
TASC	Technology Research Association for Single Wall Carbon Nanotubes
TEM	transmission electron microscope

1. Current status of working environment measurement

1.1 International trends

Currently, the measurement of airborne nanomaterials such as CNTs is performed primarily with real-time aerosol measuring instruments and through gravimetric analysis, chemical analysis, and electron microscope observation of particles collected with filters and others.

About nanomaterials

In 2008, the International Organization for Standardization (ISO) issued ISO TR12885 "Nanotechnologies—Health and safety practices in occupational settings relevant to nanotechnologies," which includes the characterization of nanomaterials in a working environment. This document provides an exhaustive summary of available characterization methods, including the measurement of mass, number, surface area concentration, and particle size distribution; it also discusses collection of samples and measurement of particles with high aspect ratios. "Approaches to Safe Nanotechnology," issued by the US National Institute for Occupational Safety and Health (NIOSH) in 2009 (NIOSH 2009), also discusses in detail the available characterization methods.

As a practical sampling strategy for the measurement of nanomaterials in working environments, certain tiered approaches have been suggested by NIOSH (NIOSH 2009; Methner *et al.* 2010a), the working party of the Organisation for Economic Co-operation and Development (OECD) (OECD 2009), and German agencies (IUTA, etc., 2011). In the proposals by NIOSH and OECD, a procedural flow has been suggested, beginning with measurements using portable real-time measuring instruments, a condensation particle counter (CPC), and an optical particle counter (OPC). If a rise in concentration is seen, more detailed measurements should be performed, including electron microscope observations, chemical analysis of particles collected by filtration, measurement of an individual's exposure, and investigation of contamination on walls and floors. NIOSH has used this method to measure emitted nanomaterials at 12 facilities that handle nanomaterials, including two facilities with multiwall CNTs (MWCNT) and two facilities with carbon nanofibers (CNF) (Methner *et al.* 2010b). CPC cannot obtain concentrations for different particle sizes. However, it can measure the total concentration of particles sized at approximately 0.01–1 μm. OPC can typically measure concentrations of particles roughly 0.3–10 μm in size. Thus, these two pieces of equipment enable particles to be measured over a wide size range—from nano- to micro-sized particles—including dispersed particles, aggregates, and agglomerates. Portable and relatively inexpensive versions of these instruments are available.

The tiered procedural flow proposed by German agencies (IUTA, etc., 2011) focuses on the measurement of emitted nanoscale particles. In this procedural flow, Tier 1 is "information gathering" to establish whether there is a possible release of nanoscale particles, and Tier 2 is "basic exposure assessment" of whether the occupational exposure limit (OEL), benchmark values, or the background is exceeded (e.g., measurement with a CPC). Tier 3 is "expert exposure assessment" by measurement with a scanning mobility particle sizer (SMPS), a fast mobility particle sizer (FMPS), or a CPC, and detailed analysis

(chemical analysis and electron microscope observation) of particles collected by filters and others.

A document issued by Safe Work Australia (The International Laboratory for Air Quality and Health 2012) created by The International Laboratory for Air Quality and Health, Queensland University of Technology, has provided application examples of measurements with a CPC, OPC, light-scattering aerosol photometer, SMPS, and nanoparticle surface area monitor (NSAM); detailed analysis (chemical analysis and electron microscope observation) of particles collected by filters has also been provided.

At the OECD working party (Steering Group 8), a guidance plan is being formulated for an exposure measurement technique that refers to the abovementioned and other documents. Furthermore, there is also continued promotion of activity aimed at internationally harmonizing the measurement of nanomaterial in working environments (Brouwer *et al.* 2012).

For trends in Japan, the Ministry of Health, Labour and Welfare, for the period FY 2011–2015, is pushing ahead with measurement method examinations and exposure field surveys for nano-TiO_2, black carbon, CNTs, fullerenes, and nanosilver (Ministry of Health, Labour and Welfare 2012). The National Institute of Occupational Safety and Health, Japan (JNIOSH) launched a three-year project "Study on collection and analysis procedures of airborne particulate matters in nanomaterial-handling workplaces (FY 2013–2015)." They are developing and evaluating methods for measuring airborne nanomaterials, including CNTs and nano-TiO_2.

About CNTs

CNTs have been measured in working environments in many cases using aerosol measuring instruments and observation of collected particles by electron microscopy and energy dispersive x-ray spectroscopy (EDX) (Han *et al.* 2008; Bello *et al.* 2008; Tsai *et al.* 2009b; Johnson *et al.* 2010; Dahm *et al.* 2013).

As a method for quantifying CNTs, NIOSH has proposed the use of thermal carbon analysis "NIOSH Method 5040," developed with the purpose of measuring organic carbon (OC) and elemental carbon (EC) such as diesel particles. NIOSH Method 5040 allows for comparison with the Recommended Exposure Limit (REL) (NIOSH 2013). NIOSH has reported measurement cases using this method at facilities that handle CNTs and CNFs and have also demonstrated its effectiveness (Birch *et al.* 2011; Dahm *et al.* 2012). JNIOSH has also performed measurements at facilities that handle CNTs using this method (Takaya *et al.* 2010; 2012).

In addition, there are cases where the detection and quantification of CNTs has been performed using the amount of metal catalysts contained as impurities within the CNT as an indicator of CNT mass (Maynard *et al.* 2004; Birch *et al.* 2011; R'mili *et al.* 2011; Rasmussen *et al.* 2013; Reed *et al.* 2013). Cases where the number concentration in air is estimated by counting the number of CNT fibers or the number of CNT agglomerates using electron microscope observations of particles collected by filters have also been reported (Han *et al.* 2008; Lee *et al.* 2010; Ogura *et al.* 2011).

Safe Work Australia (2010) has verified a CNT response specifically for 10-nm-diameter MWCNTs using an electrical low-pressure impactor (ELPI) and an SMPS. By collecting CNTs at each stage of the ELPI or with a gold-coated polycarbonate filter (pore size 100 nm; modified ISO14966 for asbestos), they

have demonstrated that it is possible to make observations with a field emission scanning electron microscope (FE-SEM).

1.2 Occupational exposure limits

Although there is no legally enforceable occupational exposure limit (OEL) for CNTs, recommended OELs have been suggested by several organizations and companies (Table 1.1). It should be noted that terminology and meaning are slightly different according to each organization and company. These OELs are determined as values of mass concentration and are often proposed for values of a respirable particle concentration (values that exclude coarse particles that do not reach the lungs; by the ISO7708 definition, 4-μm particles are reduced by 50%). CNTs often agglomerate, and many of the animal tests that are the basis of these OELs were performed using agglomerated CNTs. However, in the NEDO "Research and Development of Nanoparticle Characterization Methods" Project (no. P06041) (Nakanishi 2011), toxicological tests were performed for CNTs that had been dispersed to some extent. However, the difference in the effects of an agglomerated state is not yet clear.

For fibrous particles for which an OEL is yet to be determined, the UK's British Standard (2007) and Germany's IFA (2009) have proposed a provisional benchmark, namely 1/10 of the asbestos OEL based on the number of fibers (0.01 fibers/cm^3). However, CNTs generally exist in an agglomerated state, which is often not in the form of fibers that can be counted.

Table 1.1 OELs for CNT working environments

Source	Material	Proposed value (μg/m^3)	Comments
NEDO Project (P06041) (Nakanishi 2011)	CNT	30 (respirable particles)	This value assumes subchronic exposure 8 h/day for 5 days/week over 15 years. It is premised on a reevaluation within 10 years.
US NIOSH (NIOSH 2013)	CNT・CNF	1 (respirable particles)	Recommended Exposure Limit (REL), TWA
ENRHES Project (EC 2010)	CNT	0.7-30	Derived No effect level (DNEL)
Bayer (Pauluhn 2010)	The company's own MWCNT	50	Occupational Exposure Limit (OEL), TWA
Nanocyl (Luizi 2009)	The company's own MWCNT	2.5	

TWA: time weighted average

1.3 Current status and challenges

Appropriate metric and measurement method to manage CNT exposure

CNTs vary widely depending on factors such as tube diameter, number of layers, agglomerated state, form, and impurities (i.e., carbon that is not a CNT; catalytic metal). Such properties cannot be expressed using a single metric. In addition, the relationship between these individual properties and their harmful

effects is unclear. Although some theories propose that harmful effects are related to the surface area or volume of the material (Maynard & Kuempel 2005; Pauluhn 2011), the appropriate metric for assessing health effects is yet to be definitively determined.

Currently, the OELs for CNTs are determined as mass concentrations (Table 1.1) because toxicological tests for CNTs are performed and evaluated using mass concentrations. As CNTs have large surface area and volume per mass, mass-based OELs for CNTs are equal to or lower than the most severe value compared to the OELs for other dust (OELs from the Japan Society for Occupational Health are 30 μg/m^3 for crystalline silica and 500–3000 μg/m^3 for the 1st–3rd dust categories, as respirable particle mass). Therefore, measurements of low levels of CNT mass concentrations are required, implying that more accurate measuring technology, discrimination from background particles, and sampling over long periods of time are required.

CNTs are often agglomerated, and the currently proposed OEL is a total value including these agglomerated particles. Although the relationship between the harmful effects and agglomerated state is not yet well known, the sites and fractions of deposition in the respiratory system vary for the agglomerated size (e.g., the deposition fraction into the pulmonary alveoli for particles several tens of nanometers in size is several times higher than that of submicron to micron-sized particles). In future, as the differences in the harmful effects of the agglomerated state become better known, and as CNTs are developed to be more easily dispersed and aerosolized in a non-agglomerated form, measurement and evaluation may be required to consider the differences in the agglomerated state (i.e., particle size). Furthermore, it is possible to use metrics other than mass concentration.

Other than for comparison with an OEL, in measurements aimed at determining the generation source and evaluating the effect of exposure control measures, measuring mass concentration is not necessarily suitable. Considering currently available measurement technology, measuring number concentration may be effective, especially when obtaining size-specific data. Although it is unlikely for CNTs to be aerosolized in air as a single fiber, they do take on various agglomerated states. Thus, measuring particle sizes over a large range (i.e., nano- to micron-sized particles) is desirable.

Discrimination between target CNTs and background particles

Workplaces such as factories have various aerosol particles in the background. In addition, tasks involving CNTs may generate particles other than CNTs. Most aerosol measuring instruments cannot distinguish between CNTs and other aerosols. Therefore, it is important to compare cases with and without specific tasks being performed and to compare a point in the vicinity of the generation source with a control point. Generally, because CNTs agglomerate easily, a concentration increase is often seen with particles from the submicron to micron size. For nanoparticles, the background concentration is generally relatively high, and often no increase in concentration is observed. To determine whether nanoparticles have been released and the size distribution of released particles, a simulated emission test (often called dustiness test) in the absence of any background particles may be helpful.

Although thermal carbon analysis cannot discriminate between CNTs and other (e.g.,

combustion-derived) carbonaceous particles if they burn at a similar temperature, it is an effective method for separating and discriminating CNTs from non-carbonaceous particles. In addition, a black carbon monitor (BCM), also known as an aethalometer, is an aerosol measuring instrument with a specific response to light-absorbing substances such as carbonaceous particles. There also exists a method that measures catalytic metal as an impurity present in CNTs.

Although it costs time and effort, the most reliable way to verify the existence and form of CNTs is by observing them using an electron microscope.

Release of CNTs used as a composite material

When CNTs are used in a mixed state with a polymer as a composite material, mixed CNTs (still joined to the polymer, dispersant, or binder), unmixed (free) CNTs, and debris from the polymer itself may be released during mechanical and abrasive processing. Although the harmful effects of CNTs in a mixed state are unknown, a few reports indicate that the effect is smaller than that of unmixed CNTs (Wohlleben *et al.* 2011). It is difficult to discriminate among mixed CNTs, unmixed CNTs, and debris from the polymer itself when they are released all together. Measuring CNTs in such a state remains a challenge that must be addressed in the future. The main subject of this guide is the measurement of unmixed CNTs as a single body or as agglomerate.

A simple and inexpensive measuring method

In future, the progress of CNT applications may lead to the handling of CNTs in small business facilities, thus introducing the need for an inexpensive and simple measurement method for CNT exposure control on a day-to-day basis.

2. Method for measuring airborne CNTs

Methods for measuring airborne CNTs include on-line aerosol measurement, off-line quantitative analysis, and electron microscope observation, details of which are discussed in Sections 2.1, 2.2, and 2.3, respectively. Section 2.4 discusses the usefulness of each method with respect to their specific purpose.

2.1 On-line aerosol measurement

Table 2.1 lists commercially available portable aerosol measuring instruments that are relatively inexpensive. The measurable range of particle sizes for each of these measuring instruments is given in Fig. 2.1.

According to the US NIOSH and the OECD working party, the use of a CPC and an OPC is suggested as a preliminary investigation for an environment where nanomaterials are handled (NIOSH 2009; Methner *et al.* 2010a; OECD 2009). With the combined use of a CPC and an OPC, particles over a wide range of sizes can be measured as number concentrations because a CPC can measure the total number concentration of particles sized at approximately 0.01–1 μm and an OPC can typically measure the size-classified number concentration of particles roughly 0.3–10 μm in size. In addition to these instruments, a light-scattering aerosol photometer (hereafter, photometer) and a BCM may be effective for the measurement of CNTs. The International Laboratory for Air Quality and Health (2012) uses a photometer as a simple measuring instrument for nanomaterials. Photometers are widely used for measurement of dust in environments, including offices, industrial workplaces, and the outdoors and can measure the approximate mass concentration of aerosols, and BCMs are used to measure the mass concentration of black carbon in ambient air. In recent years, a portable commercial BCM has been developed.

A limitation of these instruments—except for the BCM—is that they cannot differentiate between CNTs and other particles. These instruments have a response to all aerosols, i.e., not only CNTs but also background particles and particles generated by the work, such as combustion-generated particles, particles generated from a motor, and those generated by wear and abrasion. On the other hand, a BCM is only sensitive to light-absorbing particles (including CNTs) and non-sensitive to most background particles. However, even a BCM cannot differentiate between CNTs and other light-absorbing particles, such as soot generated in the combustion process. In either instrument, it is important that when taking measurements at a work site, one must take into account the contribution of the background particle concentrations by comparing concentrations before or after the work (or when there is no work) with measurements taken when work is in progress. Alternatively, a comparison between the work site (near the generation source) and a control point (away from the source), and if possible, a simultaneous measurement with multiple identical devices, is desirable to evaluate increases in concentration associated with the release of CNTs. It should be noted that even for identical devices, because there may be differences in response due to instrumental deviations, it is important to examine these differences in advance by measurement with multiple devices placed side by side, and if necessary, to make corrections for producing balanced results.

To verify the size distribution of released CNTs and the response (i.e., sensitivity) of the measuring

instrument to CNTs, a simulated emission test (e.g., a dustiness test) in the absence of any background particles may be helpful. Generally, CNTs are agglomerated, and when handled as a powder (for example, unsealing, weighing, transferring, and pouring), the main release is often in the form of an agglomerated particle of submicron to micron size (Ogura et al. 2012). In that case, measurement with the OPC, photometer, or BCM, all of which are responsive to submicron- to micron-sized particles, is considered effective when detecting released CNTs.

When CNTs are handled in a more dispersed state, they may be released as smaller particles (for example, aerosolization of CNTs that are well dispersed in solution). In such a case, the use of a CPC may be effective. However, apart from a clean room environment, detecting slight emission of small particles of CNTs is often difficult because nano-sized aerosols generally exist inside a normal room, or in the outdoor air, anywhere from a few thousand to several tens of thousands per cm^3.

Although larger and more expensive than the abovementioned measuring instruments, an SMPS, a FMPS, and an ELPI are measuring instruments that can obtain number concentrations of different-sized particles, including those smaller than 100 nm. An APS is a measuring instrument that can obtain number concentrations for different particle sizes (0.5–10 μm). However, the problem of discrimination between target CNTs and background particles is similar to the abovementioned portable instruments.

An evaluation example of the response to CNTs for a BCM and a photometer, which was carried out by TASC, is presented in Section 3.3. In addition, an example of released CNT detection in the presence of background particles using a CPC, an OPC, a photometer, and a BCM is provided in Section 3.4.

Table 2.1 Portable and relatively inexpensive commercial aerosol measuring instruments

	Measured metrics	Operating principles	Usefulness
Optical particle counter (OPC)	Number concentration of particles from submicron to micron size (0.3–10 μm*)	The aerosols are measured by light scattering with a laser. Approximate particles size is obtained from the intensity of scattered light, and particle number from the count of the scattered light.	Suitable for detection of agglomerated CNTs. Number and approximate size of particles is found. Discrimination from background particles is problematic, but detecting concentration increase with the released agglomerated CNTs is often possible by size-classified concentration. US$ 5,000–20,000*.
Condensation particle counter (CPC)	Number concentration of nano- to submicron-sized particles (0.01−>1 μm*)	Basic measuring principles are the same as an OPC, but the sample air is introduced into a supersaturated atmosphere of alcohol (or water), and through alcohol (or water) vapor condensing on the particles, they grow larger. Particles smaller than those measurable with the OPC can be measured. However, particle size information is not available.	Suitable when emission of small, nano-sized particles of CNTs is expected (e.g., handling dispersed CNTs). Discrimination from background particles is problematic. US$ 10,000–15,000*.
Light-scattering aerosol photometer (photometer)	Mass concentration of submicron- to micron-sized particles (>0.1 μm*) (approx. value)	Total light scattering intensity of aerosols is detected by passing through laser irradiation. Aerosol mass concentration is roughly linearly proportional to amount of scattered light; thus, approximate mass concentration of the aerosols and relative concentration change can be measured. To obtain accurate mass concentration of target CNTs, sensitivity of the device to those CNTs must be known in advance (see Section 3.3).	If the sensitivity is properly corrected, comparison with mass-concentration based OELs is possible. Discrimination from background particles is problematic. US$ 3,000~10,000*.
Black carbon monitor (BCM) (aethalometer)	Mass concentration of black carbon (approx. value)	Mass concentration of light-absorbing particles, such as black carbon, is estimated by measuring the attenuation of a light beam transmitted through aerosol particles that are continuously collected on a filter. To obtain accurate mass concentration of target CNTs, sensitivity of the device to those CNTs must be known in advance (see Section 3.3).	If sensitivity is properly corrected, a comparison with concentration based OELs is possible. The BCM is only sensitive to light-absorbing particles (including CNTs) and not to most background particles. Sensitivity drops with particle load and changes in sensitivity may occur due to interference from scattering aerosols (see Section 3.3). US$ 10,000–*

*an approximate value that differs depending on manufacturer and performance

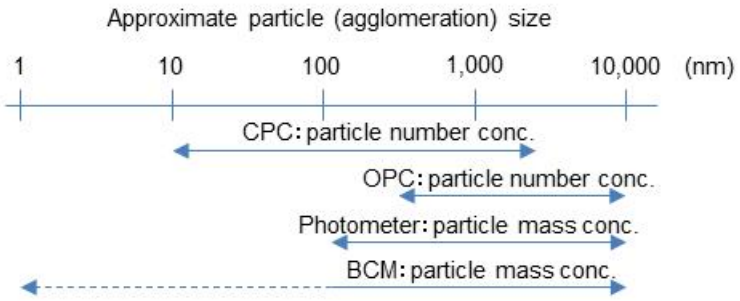

Figure 2.1 Measurable range of particle sizes for each of aerosol measuring instruments

2.2 Off-line quantitative analysis

As discussed in Section 1.2, the OELs for CNTs are currently determined using mass concentration values. Table 2.2 lists methods for quantifying CNT mass concentration. A straightforward method is to measure the mass of the CNTs collected through a filter by an ultra-microbalance (i.e., gravimetric analysis). However, separation discrimination between CNTs and background particles is not possible, and the determination limit is generally high. In many cases, quantifying CNTs as an amount of carbon using thermal carbon analysis is considered most effective. Other methods involve performing elemental analysis of a metal catalyst, which is contained as an impurity within the CNT, as an indicator of CNT mass.

In either method, the lower detection limit depends on total sampling volume (sampling flow rate × sampling time). It should be noted that comparisons with a control sample—a blank sample or a sample taken in a non-operational period and/or taken away from the generation source—are important.

Table 2.2 Off-line measuring methods for quantifying CNT mass concentrations

	Method	Usefulness
Gravimetric analysis	Aerosols collected with a filter; increase in filter mass weighed with an ultra-microbalance.	Straightforward but separation discrimination between CNTs and background particles is not possible. Determination limit is usually high. Only applicable when background particle concentration is low or the concentration of target CNTs is high.
Thermal carbon analysis	Aerosols collected by filter and combusted. By measuring CO_2 (or CH_4 obtained by reduction), CNTs are measured as quantity of carbon. The NIOSH Method 5040, IMPROVE method, etc.	Separation discrimination from background particles other than carbon is possible. Depending on heating and combustion conditions, separation from organic carbon, soot, etc. is possible to some extent. With methods such as NIOSH Method 5040 and IMPROVE method, no particular preprocessing is generally required.
Elemental analysis	Aerosols collected by filter. By measuring catalytic metal (impurity) contained in CNTs, CNT quantity is estimated. ICP-AES, ICP-MS, etc.	Applicable only when metal content is known (a constant) and is relatively high. Usually, preprocessing is required by dissolving in solution.

(a) Gravimetric analysis

Aerosols are collected with a filter not affected significantly by moisture and gas absorption (e.g., Teflon fiber), and the mass concentration of sampled aerosols is found by weighing the mass of the filter with an ultra-microbalance before and after sampling. Although this method is the most straightforward, discrimination identification between the CNTs and background particles is not possible. Therefore, it is only applicable for low concentrations of background particles, such as in a clean laboratory or when the concentrations of target CNTs are high (the background concentration of respirable particles in a general environment is typically 10−50 μg/m^3). Although the determination limit for this method is also dependent on the total sampling volume of the filter sample, it is typically of the order of several tens of μg/m^3. A measurement case performed by TASC at a work site handling CNTs is given in Section 3.5.

(b) Thermal carbon analysis

Thermal carbon analysis is a quantitative method with relatively high sensitivity and can perform separation discrimination from background particles other than carbon. It is presently considered as the most reliable quantitative measurement method for CNTs. By heating and burning a sample, the amount of carbon can be found by measuring the CO_2 (or the CH_4 obtained by reducing it).

The NIOSH Method 5040 is recommended by the US NIOSH as a method for quantifying CNTs in the air (NIOSH 2003; 2013). This method is a fractional determination method for OC and EC that was developed to measure diesel particles (Fig. 2.2). A sample collected with a quartz fiber filter is heated in stages in helium atmosphere to vaporize OC. Then, the EC is burned by heating in stages in the presence of oxygen. The vaporized or burned carbon is completely oxidized to CO_2 with a catalyst. Then by reducing it to CH_4 with a catalyst, it is detected using a flame ionization detector. CNTs are detected in the EC fraction. The background EC concentration in a general environment is typically less than a few μg/m^3. The determination limit for this method also depends on the total sampling volume of the filter sample, but is typically 1 μg/m^3. The REL of 1 μg/m^3 for CNTs proposed by NIOSH (2013) has been determined based on this determination limit.

An evaluation of CNT quantification by thermal carbon analysis carried out by TASC is presented in Section 3.1. In addition, a measurement case at a work site handling CNT is presented in Section 3.5.

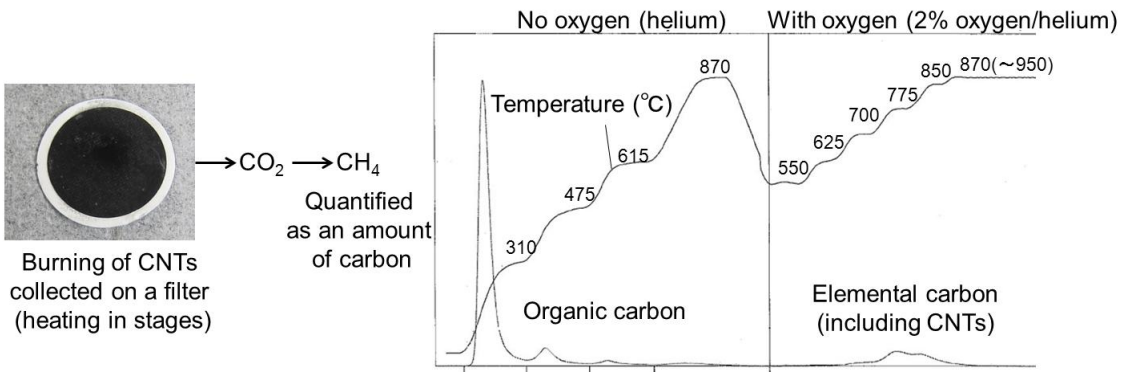

Figure 2.2 Example of thermal carbon analysis

Here, we provide several considerations regarding this method.

- When heated in stages in helium atmosphere, some of the OC is carbonized (changed into soot) and detected as EC. Usually, in thermal carbon analysis, the optical properties of a filter sample are monitored (reflection and transmission), and a correction is made assuming the carbonized organic components absorb light in the same manner as EC (called thermal–optical carbon analysis). However, if micron-sized CNT aggregates are collected in spots on a filter, the correction may not be performed properly. Furthermore, when the EC concentration is low, slight variations in the optical correction may lead to a significant error. From a safety standpoint, we should avoid underestimating the EC (i.e., CNTs); therefore, we may choose not to apply optical correction. Even without optical correction, if the soot contribution is assumed to be equal to a control sample (i.e., the presence of organic components contributing to soot generation is equal to the control sample), the soot contribution can be considered by a comparison with the control sample.
- Only a portion of a filter sample is usually analyzed at one time because the optical properties of the filter are monitored for the optical correction. Therefore, to obtain an accurate value, particles must be collected on the entire filter homogeneously (or multiple analyses are required to measure the entire filter). However, to remove coarse particles that cannot reach the lungs, when an impactor or cyclone is used and connected to a filter holder, micron-sized large CNT aggregates in particular may not be collected evenly on the entire filter as they tend to concentrate in a small area in a straight direction from the air inlet of the filter holder. In this case, an alternative method can be adopted whereby the entire filter is folded and introduced into the measuring equipment in order to measure the whole amount on the filter; even though optical correction cannot be applied. This yields no error from particles collected unevenly on the entire filter and sensitivity is improved as the absolute quantity increases. We have verified that the whole quantity of the filter can be measured by folding a filter of diameter 37 mm and putting it into the measuring equipment (Hashimoto *et al.* 2013).
- The typical heating conditions in the NIOSH Method 5040 are set as 310–870 °C in helium atmosphere, and 550–870 °C in oxygen. Under these conditions, a single measurement takes approximately 15 min. The Interagency Monitoring of Protected Visual Environments (IMPROVE)

method, widely used in the analysis of carbon components in environmental air samples, specifies different heating conditions for the NIOSH Method 5040, namely 120–550 °C in helium atmosphere, and 550–800 (or 850) °C in oxygen. Under these conditions, a single measurement takes approximately 30 min. The US NIOSH has adopted heating conditions based on the NIOSH Method 5040 for measuring CNTs, and Ono et al. of JNIOSH have adopted conditions based on the IMPROVE method (Ono-Ogasawara & Myojo 2011; Ono-Ogasawara *et al.* 2013). However, regardless of which method is used, for MWCNTs of large diameter (more than several tens of nm), the temperature must be increased (e.g., to approximately 950 °C; see Section 3.1). It is best to check the combustion temperature of the target CNTs in advance to determine appropriate heating conditions. The information on combustion temperature is also useful for discriminating the CNTs of field samples from background carbon (see Fig. 3.10 in Section 3.5).

- By the prebaking of a quartz fiber filter (e.g., 3 h at 900 °C), the blank concentration of the filter media can be reduced. However, if a filter is kept in a plastic container or filter holder for hours, the OC concentration (and the EC concentration from its carbonization) may increase.
- When CNTs are used as a composite material in a mixed state with a polymer, the CNTs may be released with the polymer, dispersant, or binder during processing and abrasion. In such a case, OC in relatively high concentration may affect the measurement of EC (i.e., CNTs) during thermal carbon analysis. Measuring CNTs in such a state remains a challenge that must be addressed in the future.

(c) Elemental analysis

CNT quantity can be estimated by collecting aerosols with a filter and taking measurements of catalytic metals (i.e., impurities in CNTs) using, for example, inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS). The metal content in the CNTs must be found beforehand, and the CNT quantity can then be calculated assuming that the content percentage is a constant even when CNTs are aerosolized. However, this method is difficult for CNTs with low or varied metal content. Example applications come from NIOSH, who estimated CNT and CNF concentration using iron and nickel as indices by using ICP-AES (Maynard *et al.* 2004; Birch *et al.* 2011). The lower limit of detection depends on metal content, amount of particles sampled, and abundance of background concentration. However, according to a report by Birch et al. (2011), the determination limit was inferior to thermal carbon analysis.

The OEL for CNTs often has been proposed as the mass concentration of respirable particles (the value excluding those coarse particles that do not enter all the way into the lungs; 4 μm particles are cut by 50% according to the ISO 7708 definition). To obtain the mass concentration of respirable particles, aerosols must be collected with a filter after removing coarse particles with a cyclone or an impactor. Ideally, to prevent loss of charged particles, the cyclone (or impactor), filter holder, and tubing should have electrical

conductivity. Note that when using an impactor, agglomerated particles may disperse with shear force due to the high-speed air flow when passing through the nozzle and collision of coarse particles against the collection plate (Yamamoto & Suganuma 1983; Yamada *et al.* 2013). Thus, some coarse particles may be collected by the filter without being removed. In that case, the respirable particle concentration will be overestimated (safest estimate). In addition, although the shear force generated by a cyclone is not as strong as the force generated by an impactor, some dispersion may still occur.

As an alternative easy method, the collection of the total particles with an open-faced filter holder rather than attempting to collect just the respirable particles may be adopted although it leads conservative estimation. When neither a cyclone nor an impactor is used, the flow rate can be set arbitrarily, which results the determination limit being lowered by increasing the sampling volume.

If a multiple stage cascade impactor is used, particles can be classified by size and collected separately. Ono et al. of JNIOSH (Ono-Ogasawara & Myojo 2011; Ono-Ogasawara *et al.* 2013) have proposed a method for the separation discrimination of CNTs and combustion-derived background EC by determining the EC concentration for different particle sizes using a cascade impactor.

Rather than assessing particles in air, assessing particles deposited on the floor or walls by thermal carbon analysis or elemental analysis may also be helpful for evaluating the state of contamination over a long period of time.

2.3 Electron microscope observation

Although it costs time and effort, the most reliable way to verify the existence and form of CNTs is by observing them using an electron microscope. Electron microscopes available for CNT observation include a scanning electron microscope (SEM) (typically a field-emission SEM (FE-SEM)) and a transmission electron microscope (TEM). Whether each individual fiber (i.e., a single tube) of CNTs can be seen depends on the performance of the electron microscope and the tube diameter of CNTs. Resolution is generally higher for TEMs than for SEMs. Observing individual fibers of narrow CNTs (especially SWCNTs) is often difficult for SEMs because of their lower resolution and also for TEMs because of the interference of the support film on the TEM grid. On the other hand, SEMs are generally suitable for observations of agglomerated CNTs.

With either SEMs or TEMs, verifying the form and visibility of target CNTs in advance makes it easier to identify the CNTs from the collected aerosols. In many cases, it seems possible to distinguish CNTs from other particles by their characteristic form. For CNTs that include catalytic metal, more accurate identification may be facilitated by using EDX for elemental analysis, which is an optional system with SEMs and TEMs.

The success of electron microscope observation largely depends on particle sampling methods. The particle sampling methods for SEMs are generally easier than those for TEMs. In a TEM case, it is necessary to load the aerosol CNTs on the grid used for the TEM observations. Relatively simple methods are listed in Table 2.3.

Table 2.3 Relatively simple particle sampling methods for electron microscope observation

	Method	Usefulness
Polycarbonate filter	Polycarbonate filters having a flat surface and many holes (pores) of fixed size are used for collecting aerosol particles.	For SEM Particle collection efficiency is relatively high. Easy
Impactor	An impactor collects particles by inertial impaction. Particles can be collected on a TEM grid by attaching it to the surface of the collection plate.	For TEM (and SEM) Particles can be classified by size. Particles can be collected on a TEM gird at a high density; this may, however, cause particles to overlap. Difficult to collect smaller particles.
Porous TEM grid	Air is passed through a porous TEM grid to collect aerosol particles on it.	For TEM Easy

(a) Polycarbonate filter

Aerosol particles are collected by means of a polycarbonate filter having a flat surface and many holes (pores) of fixed size. Since the polycarbonate filter itself is nonconductive, a coating of conductive layer on the filter (e.g., gold or platinum vapor deposition) is required either before or after sampling particles in order to prevent charge-up when performing observations with a SEM. Observations can be made by fixing a portion of a filter sample to a stage with a conductive

double-sided adhesive tape. Polycarbonate filters with pore diameters down to a few tens of nanometers are commercially available, and although the trapping efficiency increases for filters with smaller pores, the achievable air flow rate is reduced with the higher pressure drop as pore diameters decrease. Even particles smaller than the pore diameter are collected on the filter to some extent because of interception, inertial impaction, and diffusion. For a stainless-steel filter holder with an effective filtering area of 3.7 cm^2 using a polycarbonate filter with 80 nm pores of pore density of $6 \times 10^8/cm^2$ and sampling at a flow rate of 0.3–1 L/min, the particle sampling efficiency on the filter surface is greater than 60%, even for spherical particles of 30 nm at which filter efficiency almost reaches a minimum (unpublished TASC data). For non-spherical particles such as CNTs, sampling efficiency is expected to be higher than that for spherical particles because of particle interception. Example SEM observations of CNTs collected with a polycarbonate filter are shown in Fig. 3.4 in Section 3.2 and Fig. 3.11 in Section 3.5.

(b) Impactor

Using an impactor, which collects particles by their inertial impaction, particles can be collected on a TEM grid by attaching it to the surface of the collection plate (Birch *et al.* 2011). If a multiple stage cascade impactor is used, particles can be classified by size and collected separately. Particles can be collected and concentrated on a small area of the collection plate, making it possible to collect particles on a TEM gird at a high density in a short time; this may, however, cause particles to overlap on the collection surface. Furthermore, agglomerated particles can break up with the acceleration and impaction. To collect smaller particles (e.g., <100 nm), higher air velocity with a lower pressure is required, which means that a large vacuum pump is required.

(c) Porous TEM grid

A method to collect aerosols on a TEM grid has been developed and proposed by the research group at INERIS (French National Institute for Industrial Environment and Risks) (R'mili *et al.* 2013), in which air is passed through a porous TEM grid (Lacey, Holey, Quantifoil, etc.) (Fig. 2.3). For the porous TEM grid (Quantifoil) with a pore diameter of 1.2 μm (1.3 μm in TEM observations) and pore density of 1.3×10^7 pores/cm^2, the sampling efficiency of particles of size 5–150 nm at a flow rate of 0.3 L/min has been reported as 15–18% for particles of around 30 nm with minimum efficiency (R'mili *et al.* 2013). Pore diameters less than 1 μm are commercially available, but at present, there can be large variation in the actual pore size depending on the lot.

Example TEM observations of CNTs collected with a porous TEM grid are shown in Fig. 3.5 in Section 3.2.

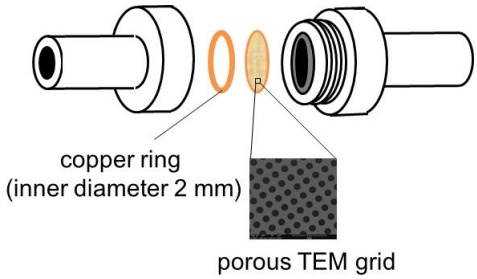

Figure 2.3 Collection of CNT with a porous TEM grid

There are also other methods, such as collection of particles by an electrostatic precipitator (Ku et al. 2007; Bello *et al.* 2008), thermophoretic precipitation (Bello *et al.* 2008; R'mili *et al.* 2011), or Brownian motion (Tsai *et al.* 2009a,b) and a filter dissolution method (used to measure asbestos; the filter is dissolved after particle collection and the particles are transferred to a TEM grid) (Han *et al.* 2008; Methner *et al.* 2010b; Dahm *et al.* 2012). Essentially, samples (and their methods) collected for TEM observation are also suitable for SEM observation.

Rather than assessing particles in air, assessing particles deposited on the floor or walls by SEM/TEM observation may also be helpful for evaluating the state of contamination over a long period of time. For example, it is possible to collect particles deposited on the floor and walls by using a conductive double-sided tape for SEM observations.

Although it costs time and effort, the number concentration of CNTs in the air can be estimated by calculation from the total sampling volume, sampling efficiency, sampling area, the total area observed by an electron microscope, and the number of detected CNTs. However, because the particle sampling efficiency generally depends on the particle (agglomerate) size, a quantitative evaluation is often difficult. To avoid underestimation, the calculation based on the minimum sampling efficiency may be adopted. In addition, when verifying the absence (and presence) of CNTs in the air, the lower limit of detection calculated by the minimum sampling efficiency should be given (Ref.: ISO 10312).

2.4 Usefulness of individual measurement methods according to their purpose

The advantages, disadvantages, and usefulness of each of the measuring methods given in Sections 2.1–2.3 are summarized in Table 2.4. In addition, application examples for individual measurement methods are given in Fig. 2.4 with respect to the purpose of measuring airborne CNTs.

Table 2.4 Advantages, disadvantages, and usefulness of individual measurement methods

	Advantage	Disadvantage	Usefulness
On-line (portable) aerosol measurement	Easy, inexpensive, time response, real time	Discriminating from particles other than CNTs	Grasp of spatial–temporal distribution, daily monitoring
Off-line quantitative analysis	Quantitative determination (by mass), CNT identification	Sampling over long periods, expensive equipment	Comparison with OEL
Electron microscope observation	CNT identification, morphology observation	Particle collection, observation cost (effort, time)	Verifying existence of CNTs, understanding the shape

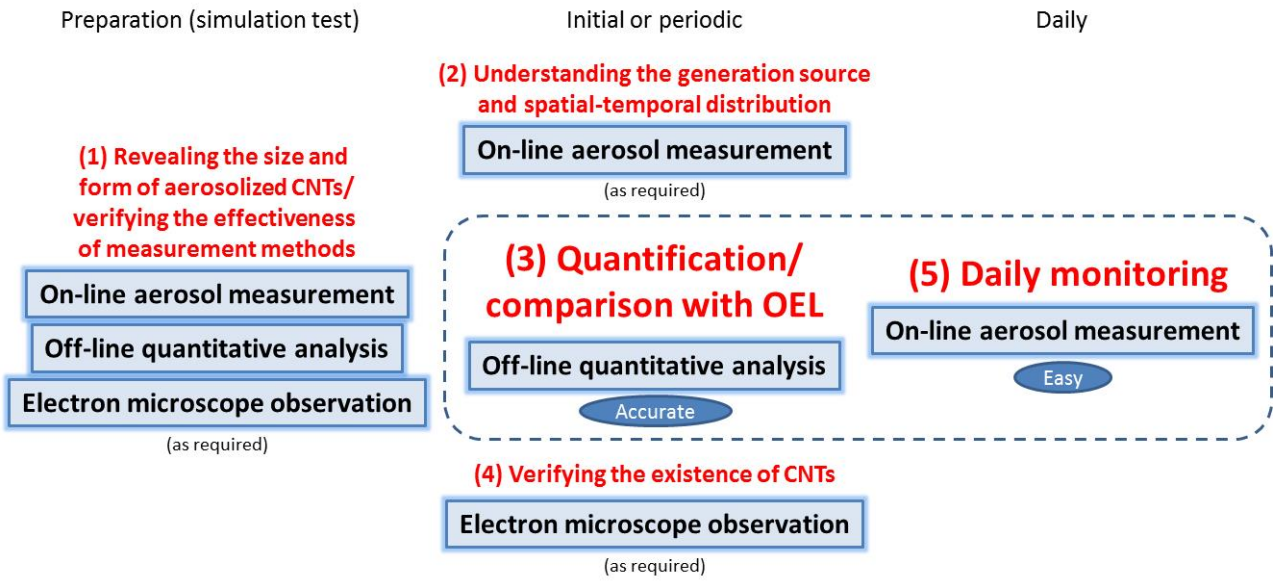

Figure 2.4 Application examples of individual measurement methods according to the purpose of measuring airborne CNTs

Explanations for numbered items (1−5) in Fig. 2.4 are provided below.

(1) Revealing the size and form of airborne CNTs and verifying the effectiveness of measurement methods

As necessary, with a simulation test performed beforehand, we can glean the size and form of airborne CNTs and verify the effectiveness of the measurement. Measurement of CNTs at an actual work site is often difficult because various aerosol particles exist in the background. Therefore, if we can determine how easily the target CNTs is aerosolized and the size distribution and form of the airborne CNTs with a

simple simulation test under laboratory conditions with no (or very few) background particles, it is possible to determine effective measurements or preventative measures. For example, if the airborne CNTs are primarily micron-sized agglomerated particles, measurements and preventative measures appropriate for micron-sized particles can be selected. In addition, by verifying in advance if the CNTs are actually measurable with each measurement method and how responses can be expected, a more accurate measurement at an actual work site will be possible.

As examples of such simple simulation tests carried out by TASC, Section 3.2 provides a measurement example of the particle size distribution and form of CNTs aerosolized by vortex shaking. Section 3.3 gives a method for evaluating the response of a BCM and a photometer to airborne CNTs, and Section 3.4 gives an example of simulating transfer performed inside a glove box.

(2) Understanding the generation source and spatial–temporal distribution

As necessary, using aerosol measuring instruments, the presence or absence of aerosol emissions can be determined in addition to spatial and temporal distribution of the concentration (association with location, time, and work task). The results in (1) can be used as a reference for the choice of the aerosol measuring instrument and its response to CNTs. However, aerosol measuring instruments have an inherent problem: the difficulty in differentiating CNTs from other particles. When there are aerosol emissions other than CNTs or the background concentration is relatively high and the concentration of airborne CNTs is low, detecting CNTs is probably difficult using aerosol measuring instruments. However, aerosol measuring instruments can obtain concentration data in units of seconds or minutes; therefore, it is suitable for temporal particle emissions and understanding the changes in concentration corresponding to each work task. A comparison with the background concentration is important, and ideally sampling with a control point should be done at the same time.

(3) Quantitative determination of CNTs and comparison with the OEL

The CNT concentrations in the air are quantified by off-line quantitative analysis (e.g., thermal carbon analysis) of collected aerosol samples, and then compared to the OEL for CNTs. The results from (2) can be referenced to set the sampling point and the time. Since the OEL is often proposed for values of a respirable particle concentration, particles are collected with a filter after first removing the coarse particles with a cyclone or impactor. Alternatively, for a safer and more conservative estimate, the total particles can be collected with a filter without using either a cyclone or an impactor. Small-scale portable cyclones and impactors for respirable particles and pumps with flow control functions are available commercially and can be used to measure either individual exposure concentrations of workers (e.g., personal breathing zone samples) or the environmental concentration in the workplaces (i.e., area samples).

To obtain values above the determination limit, in many cases particles have to be collected over a few hours. The quantitative value of CNTs obtained is the average concentration over time. As is necessary, information about the concentration variation over time could be obtained by measuring with an aerosol measuring instrument at the same time as the collecting filter samples. If the relationship between the

quantitative value of CNTs and the concentration found with the measuring instrument is understood, the approximate CNT concentration can be obtained with the aerosol measuring instrument, which can be useful for daily monitoring (5). Furthermore, by simultaneously verifying the existence of CNTs by observations with an electron microscope (4), we can determine if the concentration obtained is actually derived from the CNTs. For example, in thermal carbon analysis, other carbons (such as EC from combustion) may be detected in addition to the CNTs. In particular, soot may be generated from synthesis reactors.

When concentrations that include both CNTs and background particles are below the OEL, there is no problem. However, when those exceed the OEL, a comparison with a control sample will be important to determine the individual portions contributed by CNTs and background particles.

(4) Verifying the existence and form of airborne CNTs by observations with an electron microscope

The existence and form of airborne CNTs can be verified as necessary by observation with an electron microscope. The results from (2) and (3) can be used as a reference to set the sampling points and time. Electron microscope observations are effective in verifying that the concentration obtained (e.g., with thermal carbon analysis) is actually attributed to CNTs or identifying CNT form. CNTs may be detected through electron microscope observations even when concentrations are below the detection limit of thermal carbon analysis, although this depends on the amount of collected CNTs and the total area observed by an electron microscope.

(5) Daily monitoring

Quantitative determination (3) or electron microscope observations (4) are not realistic methods for daily monitoring. Therefore, for daily exposure management, aerosol measuring instruments could be helpful in acquiring measured values easily and in real time. In a worst case scenario, CNTs released inadvertently (e.g., neglecting to turn on a switch or malfunction of local exhaust equipment) could possibly be detected in real time by an aerosol measuring instrument. The results of (1) and (2) should serve as a reference when selecting measuring instruments. If it has already been established how the values displayed on an aerosol measuring instrument relate to the CNT concentrations from (1) or (3), the approximate concentration of CNTs can be obtained using the aerosol measuring instrument. However, if there are to be any significant changes in the process and work tasks (or at a regular interval), it would be sensible to take detailed measurements according to (3) (or (4)).

With the object of safety management of CNTs, a major concern is a comparison with the OEL in most cases; therefore, (3) and (5) in Fig.2.4 can be considered important. An example of practical methods for measuring airborne CNTs with the object of safety management of CNTs is given in Fig. 2.5. For accurate quantitative determination of CNTs and comparison with the OEL, thermal carbon analysis is effective in many cases. However, this method is not necessarily suitable for daily exposure control because they

require filter collection of particles, typically for a few hours, and the instruments are relatively expensive. For daily exposure control, portable aerosol measuring instruments (e.g., BCM) are preferable. These instruments have the ability to obtain real-time results in situ. An appropriate combination of an accurate detailed method and a simple real-time method is a reasonable way for continued management of CNT exposure.

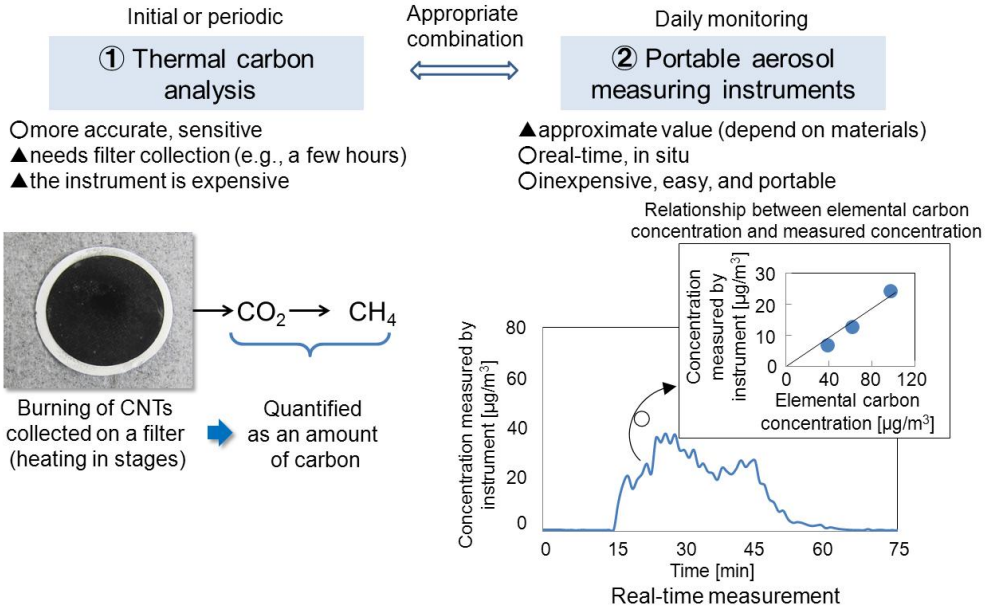

Figure 2.5 An example of practical methods for measuring airborne CNTs with the object of safety management of CNTs

3. Measurement cases

Here, we present the measurement cases that were performed by TASC.

3.1 Evaluation of CNT quantification by thermal carbon analysis

To evaluate the quantification of CNTs through thermal carbon analysis, the EC mass of approximately 100 μg of CNT powder placed in an Au (or Pt) foil boat was measured by a thermal carbon analysis instrument (CAA-202M-D, Sunset Laboratory Inc., USA) and compared with the mass of CNT powder gravimetrically measured by an ultra-microbalance (Hashimoto *et al.* 2013). The thermal carbon analysis instrument was calibrated using sucrose and glucose, and we confirmed that the instrument had a linear response within a range of 5–100 μg of carbon.

The temperature step program (Table 3.1; see also, Fig. 2.2 in Section 2.2) was essentially based on the NIOSH analytical method. However, for MWCNTs with thick tube diameter that were not oxidized at 870 °C for 120 s during the final step, the temperature and duration of the last two steps of the analytical program were set at 920 °C for 480 s and at 950°C for 480 s, referring to Myojo et al. (2009). All detected ECs were identified as CNTs. The EC detection fractions with combustion temperature are shown in Fig. 3.1.

The obtained ratios of the EC mass to the overall CNT mass (i.e., carbon purity) are shown in Table 3.2. They were consistent with or slightly lower than the carbon purity reported by the manufacturers and others. These results were reasonable because the carbon purity obtained through thermal carbon analysis in this study was the EC content per unit mass of non-pretreated CNT powder, which likely contains adsorbed water and volatile gas, whereas the reported carbon purity is typically based on the residual mass measured by thermogravimetric analysis, corrected for the initial weight loss due to moisture in the sample. Thus, thermal carbon analysis is considered capable of quantifying CNTs.

Table 3.1 Temperature step program of thermal carbon analysis

	SWCNTs & narrow MWCNTs *		thick MWCNTs	
Carrier gas	Time (s)	Oven Temperature (°C)	Time (s)	Oven Temperature (°C)
He	80	310	60	310
He	80	475	60	475
He	80	615	60	615
He	100	870	110	870
He	45	550	45	550
2% O_2/He	45	550	45	550
2% O_2/He	45	625	45	625
2% O_2/He	45	700	45	700
2% O_2/He	45	775	45	775
2% O_2/He	45	850	45	850
2% O_2/He	120	870	480	920
2% O_2/He	–	–	480	950

*NIOSH5040 equivalent program

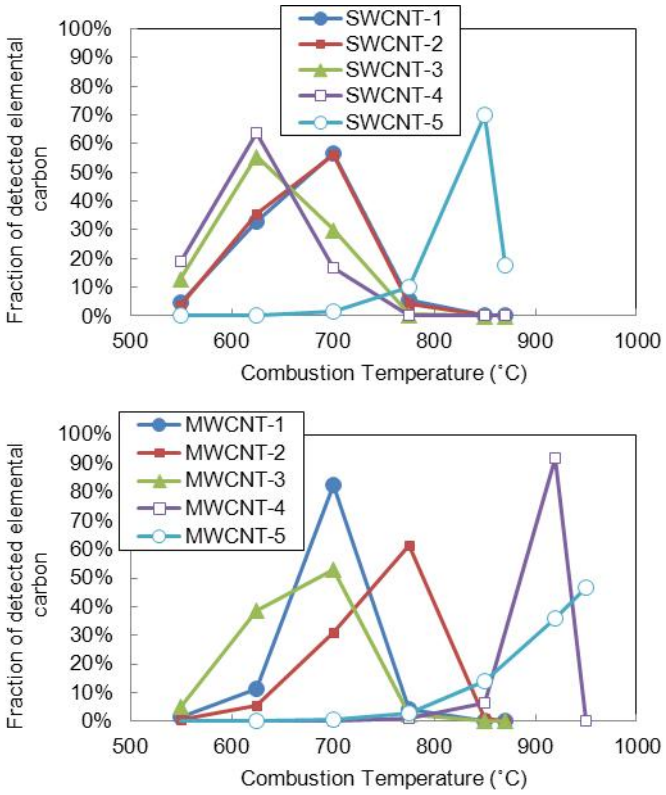

Figure 3.1 Fraction of elemental carbon (CNTs) detected with combustion temperature: SWCNTs (top) and MWCNTs (bottom)

Table 3.2 Evaluation of CNT quantification by thermal carbon analysis

	Product name, grade, process	Tube diameter [a] [nm]	Carbon purity [a]	Carbon purity by thermal carbon analysis [b]
SWCNT-1	NIST SRM2483	0.69–1.0	93% (TGA)	76±0.52%
SWCNT-2	Aldrich 704113, SWeNT, CG 100, CoMoCAT	0.7-1.3	>90% (TGA)	78±0.42%
SWCNT-3	NanoIntegris, Super pure, HiPco	0.8–1.2	>95% (TGA)	76±0.76%
SWCNT-4	Nanocyl, NC1000, CVD	2	≥70% (TGA)	65±0.63%
SWCNT-5	AIST Super- growth	3	99% (TGA)	96±0.64%
MWCNT-1	Aldrich, 724769, SWeNT SMW 100, CoMoCAT	6–9	>95% (TGA)	95±0.21%
MWCNT-2	Nanocyl, NC7000, CVD	9.5	90% (TGA)	83±1.4%
MWCNT-3	CVD	13	≥95% (ashing)	82±7.6%
MWCNT-4	CVD	44	>99.9% (metal content: 326 ppm)	100±0.54%
MWCNT-5	CVD	70	>99% (fluorescence X-ray analysis)	98±0.83%

Ref: Hashimoto *et al.* (2013)

[a] Values here typically represent those provided by the manufacturer.

[b] mean ± standard deviation (n=3–7) obtained through thermal carbon analysis.

NIST: National Institute of Standards and Technology; AIST: National Institute of Advanced Industrial Science and Technology; SWeNT: SouthWest NanoTechnologies; CoMoCAT: cobalt–molybdenum catalyst process; HiPco: high-pressure carbon monoxide process; CVD: chemical vapor deposition process; TGA: Thermogravimetric analysis.

3.2 Verification of particle size distribution and form of airborne CNTs with a simulated emission test

To verify the distribution of particle sizes of airborne CNTs, the CNTs were aerosolized by vortex shaking (Maynard *et al.* 2004; Ogura *et al.* 2009) (Fig. 3.2), and the number concentration and size distribution of the aerosolized particles were measured using an SMPS (model 3936L72, TSI Inc., USA), an APS (model 3321, TSI Inc., USA), and an OPC (model 3330, TSI Inc., USA) (Hashimoto et al. 2013); results are shown in Fig. 3.3. The distribution of particle sizes spanned a broad range, from nano to micron size.

Furthermore, to verify the form of the airborne CNTs, a polycarbonate filter with vapor-deposited platinum/palladium of approximately 2-nm thickness (Nuclepore membrane, pore diameter 80 nm, 6×10 pores/cm^2 density, and diameter 25 mm) was inserted into a stainless steel filter holder (effective filtration area 3.7 cm^2), and the airborne CNTs were collected at a flow rate of 0.5 L/min. Fig. 3.4 shows examples of the obtained SEM micrographs. In addition, by inserting a porous TEM grid (Quantifoil R0.6/1, pore diameter 0.6 μm (actually, slightly large), 3.9×10^7 pores/cm^2 density, and diameter 3.05 mm) into a stainless steel specialized holder (Mini-Particle Sampler: MPS®, Ecomesure, Janvry, France) with a copper ring (inner diameter 2 mm, outer diameter 3.05 mm), the airborne CNTs were also collected at a flow rate of 0.3 L/min. Figure 3.5 shows examples of the obtained TEM micrographs. Many of the collected CNTs were submicron- and micron-sized agglomerated particles. The CNTs appear different according to their type and tube diameter. SWCNTs with a fine tube diameter showed a net-like or flock-like form, and the MWCNTs with a narrow tube diameter showed a wool-like form. On the other hand, the MWCNTs with thick tube diameter showed a rod-like form.

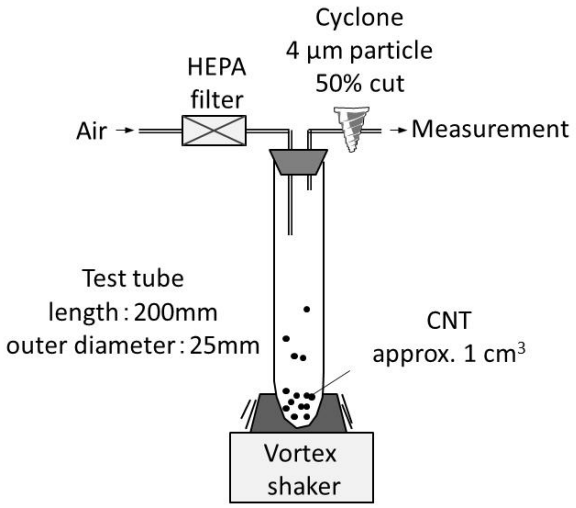

Figure 3.2 CNT aerosolization by vortex shaking
Ref.: Maynard *et al.* (2004); Ogura *et al.* (2009)

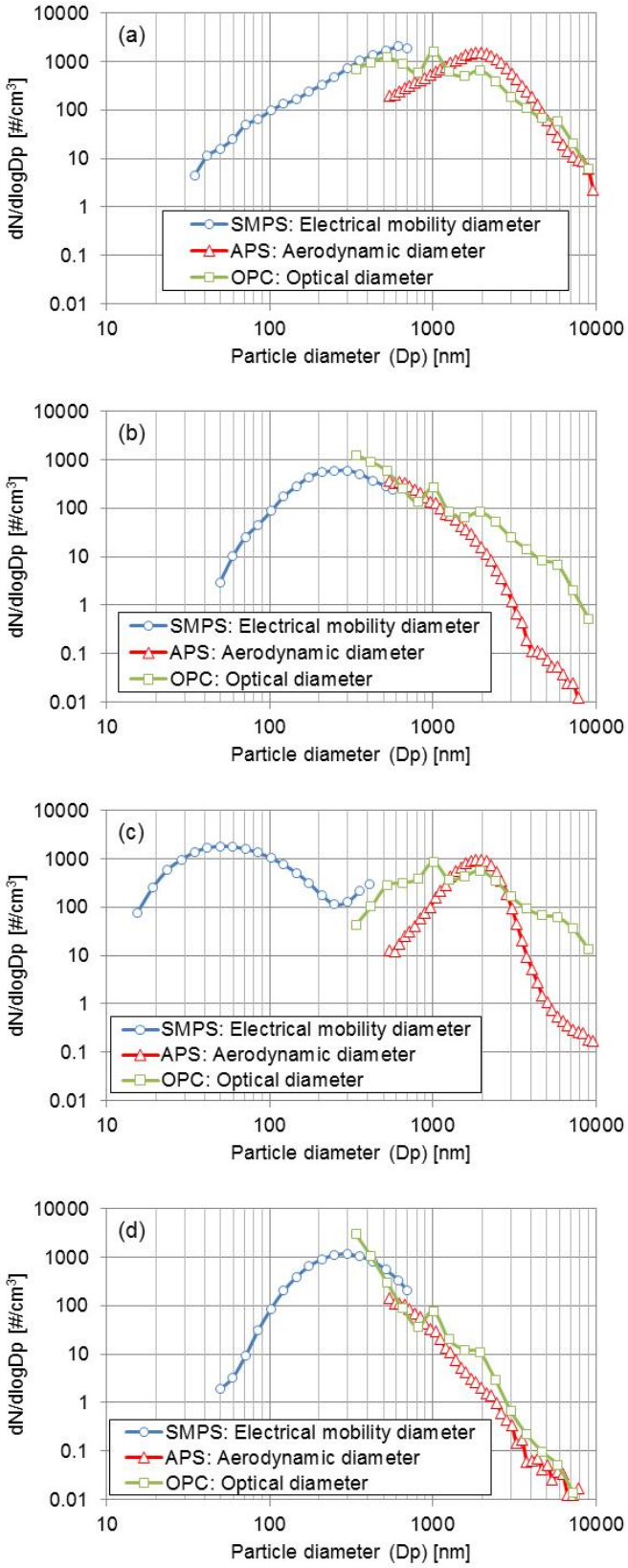

Figure 3.3 Number-based size distributions of CNTs aerosolized by vortex shaking
Particle size is the equivalent spherical diameter based on the measurement principles of each instrument
(a) Sigma-Aldrich SWeNT CG 100 SWCNTs (Tube diameter: 0.7-1.3 nm); (b) NanoIntegris HiPco SWCNTs (Tube diameter: approx. 1 nm); (c) MWCNTs (Tube diameter: approx. 13 nm); (d) MWCNTs (Tube diameter: approx. 50 nm)
Ref.: Hashimoto et al. (2013)

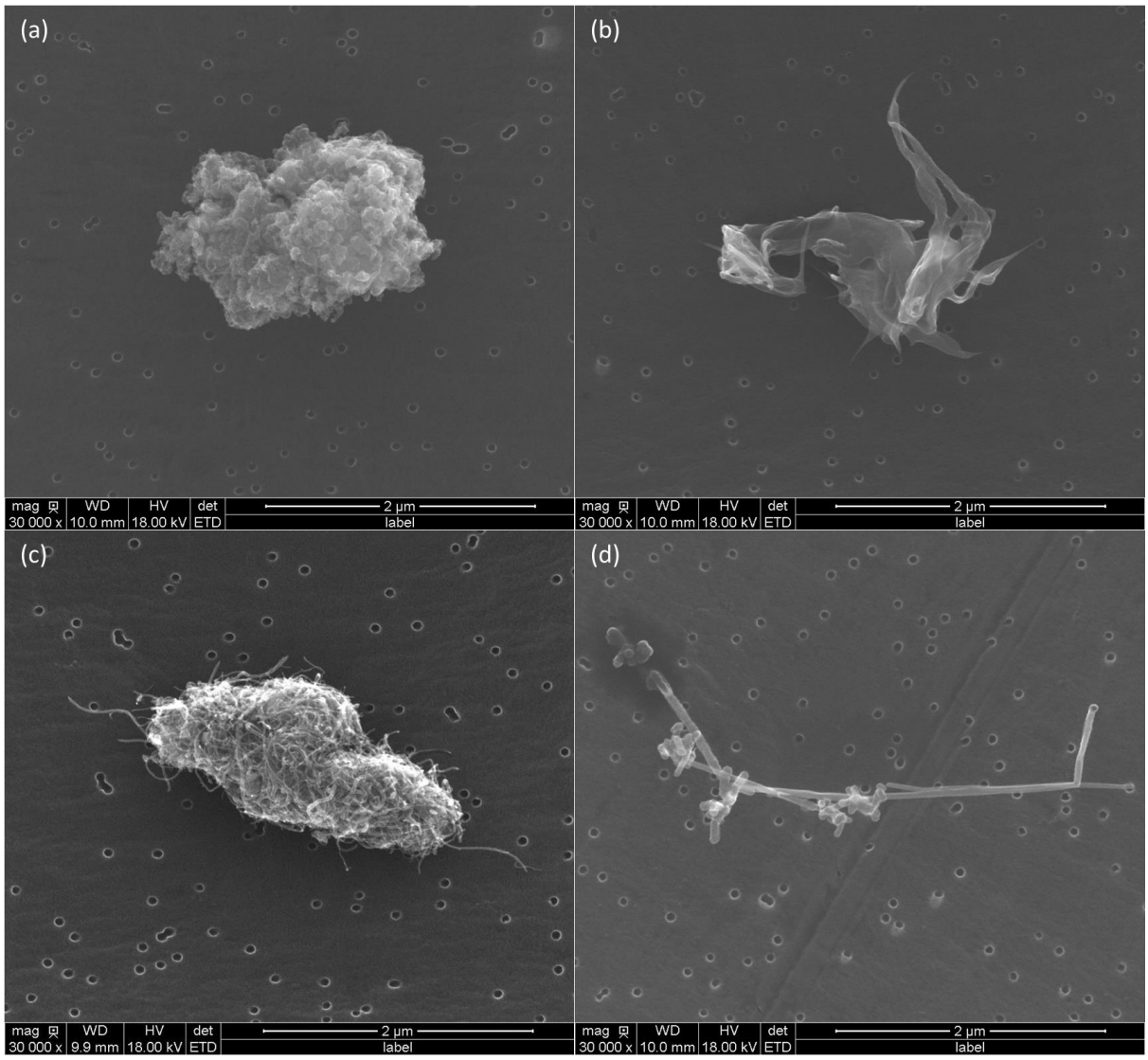

Figure 3.4 SEM micrographs of airborne CNTs collected using a polycarbonate filter
(a) Sigma-Aldrich SWeNT CG 100 SWCNTs (Tube diameter: 0.7-1.3 nm); (b) NanoIntegris HiPco SWCNTs (Tube diameter: approx. 1 nm); (c) MWCNTs (Tube diameter: approx. 13 nm); (d) MWCNTs (Tube diameter: approx. 50 nm)

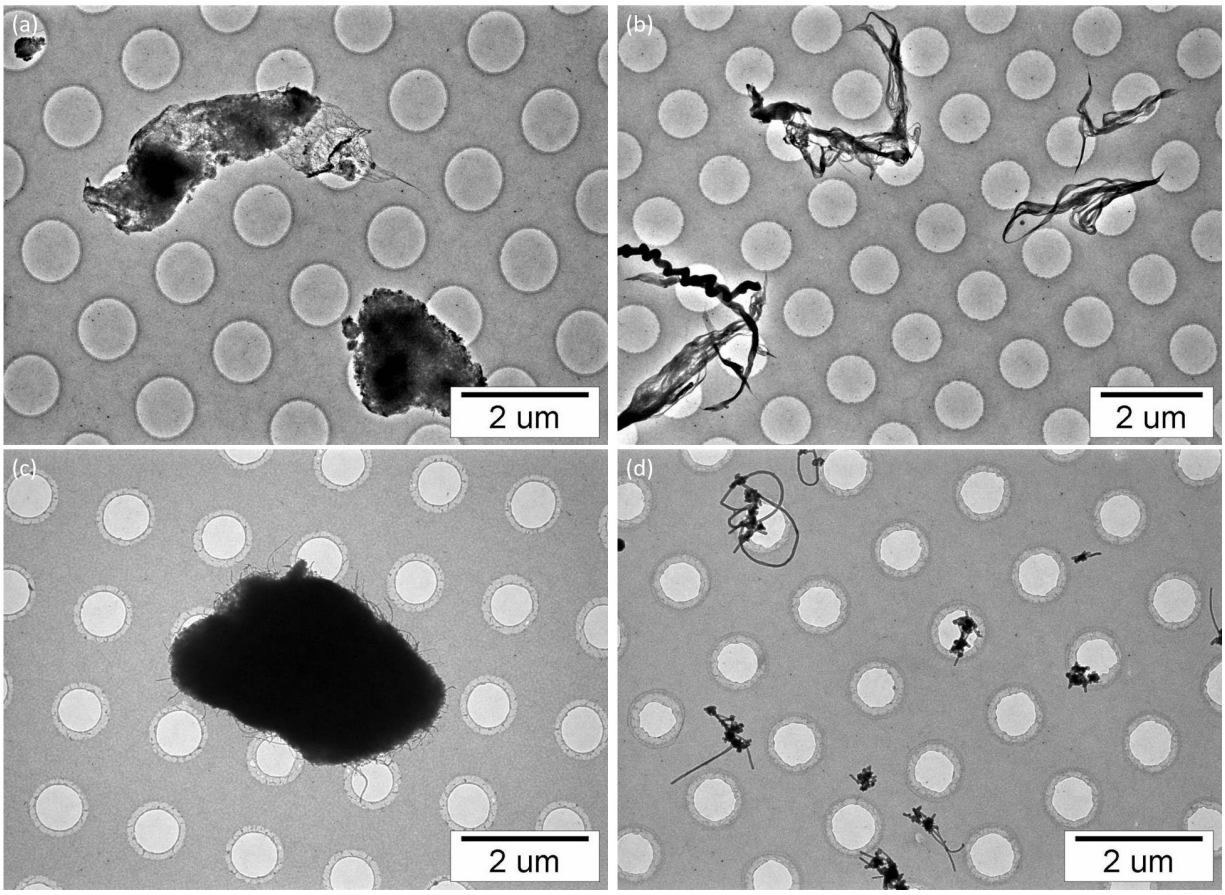

Figure 3.5 TEM micrographs of airborne CNTs collected using a porous TEM grid
(a) Sigma-Aldrich SWeNT CG 100 SWCNTs (Tube diameter: 0.7–1.3 nm); (b) NanoIntegris HiPco SWCNTs (Tube diameter: approx. 1 nm); (c) MWCNTs (Tube diameter: approx. 13 nm); (d) MWCNTs (Tube diameter: approx. 50 nm)

3.3 Evaluation of BCM and photometer responses to airborne CNTs

The responses of a BCM and a photometer to airborne CNTs were evaluated (Hashimoto *et al.* 2013). The CNTs aerosolized by vortex shaking (refer to Fig. 3.2) were measured simultaneously using a BCM (microAeth® Model AE51, AethLabs, USA; wavelength 880 nm) and a photometer (Dusttrak II 8530, TSI Inc., USA). In addition, CNTs were collected with a quartz fiber filter (37-mm diameter) for comparison (fixed inside the photometer), and the CNTs were quantified as EC with a thermal carbon analysis instrument (CAA-202M-D, Sunset Laboratory Inc., USA). The aerosolized large particles were cut using a cyclone (for respirable particles: 4 μm particles were cut by 50%). The geometric mean aerodynamic diameters for the majority of the tested CNTs were 1–4 μm. The aerosolized CNT concentrations were roughly set according to the dilution, agitation speed, and agitating with or without zirconia beads. Five SWCNT samples and five MWCNT samples were used in this study.

The responses of the BCM and the photometer to CNTs appear to be linear with respect to the EC concentration obtained by thermal carbon analysis (Fig. 3.6). However, the response factors, which are the ratios of the concentrations measured by the instrument (BCM, photometer) to those obtained through thermal carbon analysis, differed depending on the CNT samples. In many cases, the response factors were approximately 0.1–1 for BCM and approximately 0.1–2 for photometer. A response factor less than 1 results in an underestimated CNT concentration. The response of these instruments tended to depends on particle size and decrease with increasing agglomeration sizes of airborne CNTs (Fig. 3.7).

The BCM was calibrated with the black carbon concentration in the presence of coexisting (interfering) light scattering aerosols by the manufacturer. Under conditions with relatively few coexisting particles, a low response has been reported (Petzold *et al.* 1997). For the photometer, the difference in the refractive index compared with Arizona test dust (ISO 12103-1, A1 test dust), which was used for calibrating this instrument, is a contributing factor to the difference in the response.

Furthermore, the response of the BCM tended to drop with an increasing filter load. Even at approximately 1/10 of the manufacturer's recommended filter exchange frequency, a drop in the response of several tens of percent was observed. The reason might be attributed to the clean environmental conditions (i.e., the absence of interfering light-scattering materials). Thus, in a relatively clean working environment or when the CNT concentration is relatively high, a similar tendency may be seen.

From the above results, we can summarize the following points to consider when using these instruments.

- The raw readings given by a BCM and a photometer calibrated by their manufacturers have the potential to underestimate CNT concentration (especially for large agglomerated CNTs). By determining the response factor for target CNTs beforehand through the method presented here, it is expected to enhance the measurement accuracy of these instruments.
- With a BCM, in relatively clean environments or when CNT concentration is relatively high, even for loads of approximately 1/10 of the manufacturer's recommended filter exchange frequency, the response may possibly drop by several tens of a percent. Therefore, it is better to change the filter more frequently or to take the drop in the response into account in advance.

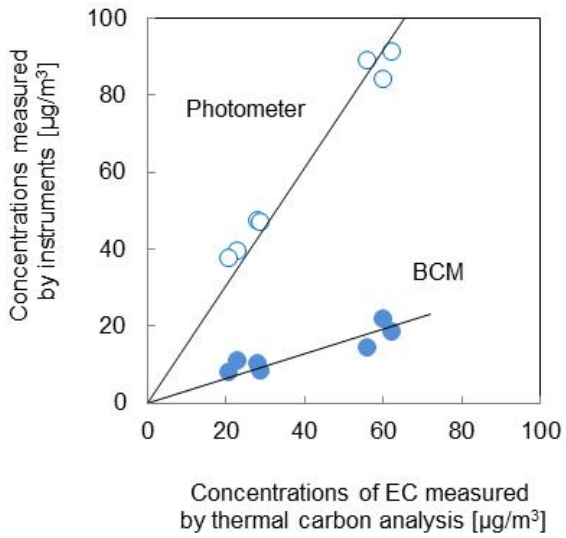

Figure 3.6 Responses of the BCM and the photometer to airborne CNTs compared to the CNT mass concentrations measured by thermal carbon analysis.
AIST Super-growth SWCNT
Ref.: Hashimoto et al. (2013)

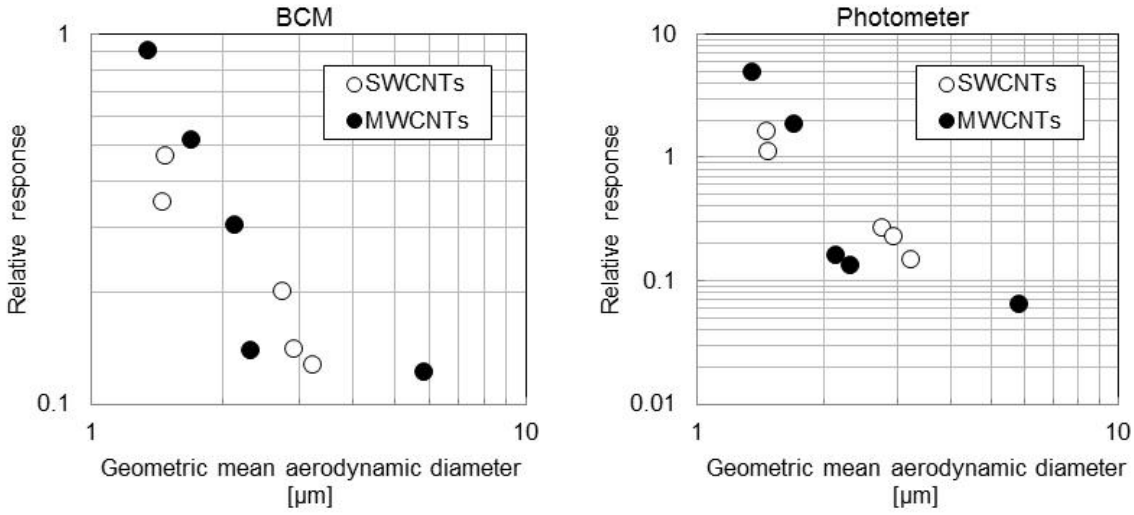

Figure 3.7 Relationships between the geometric mean aerodynamic diameters of aerosolized CNTs to the relative responses of the BCM (left) and the photometer (right).
Ref.: Hashimoto et al. (2013)

3.4 Measurement when simulating handling CNTs

Regarding the measurement of airborne CNTs in the presence of background aerosols using portable aerosol measuring instruments, the measurements were conducted when simulating handling CNTs. Inside a glove box in which background particles (from the outside atmosphere) are introduced, a simulated task of transferring approximately 100 cm^3 (approximately 8 g) of MWCNTs (SWeNT SMW 100, Sigma-Aldrich; tube diameter: 6–9 nm) to another container was repeated every minute over a period of 30 min (Fig. 3.8). The aerosols in the glove box were measured continuously using a CPC (model 3007, TSI Inc., USA), an OPC (model 3330, TSI Inc., USA), a photometer (Dusttrak II 8530, TSI Inc., USA), and a BCM (microAeth® Model AE51, AethLabs, USA; wavelength 880 nm). For comparison, CNTs were collected with a quartz fiber filter (37-mm diameter; fixed inside the photometer), and the CNTs were quantified as EC using a thermal carbon analysis instrument (CAA-202M-D, Sunset Laboratory Inc., USA).

Figure 3.9 shows the temporal variation in the concentration measured by each instrument. For diameters greater than 0.47 μm with the OPC and for the photometer and BCM, an increase in concentration was observed during the transfer task (i.e., from 15:30 to 16:00). However, for diameters of 0.3–0.47 μm with the OPC and for the CPC, no increase in concentration associated with the task was observed. Since CNTs agglomerate easily, a concentration increase is often seen with particles from the submicron to micron size. On the other hand, the background concentration for nano-sized particles is generally relatively high, and often no increase in concentration is observed. When CNTs are released primarily in an agglomerated state and the background concentration is relatively high, the OPC and the BCM may be effective for measuring airborne CNTs in terms of discrimination from background particles.

It is noted that the CNT concentration in the air determined by thermal carbon analysis of the CNTs collected in the filter (calculated as the average value over a total of 40 min; 30 task minutes + the following 10 min) was approximately 300 $\mu g/m^3$. If we understand the relationship between CNT concentrations measured by the portable measuring instruments and the concentrations measured by thermal carbon analysis, we can reasonably predict CNT concentrations from the measurement by portable measuring instruments.

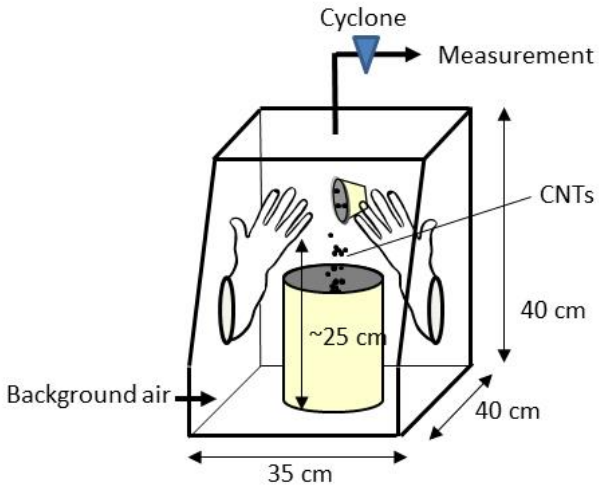

Figure 3.8 Simulated transfer task

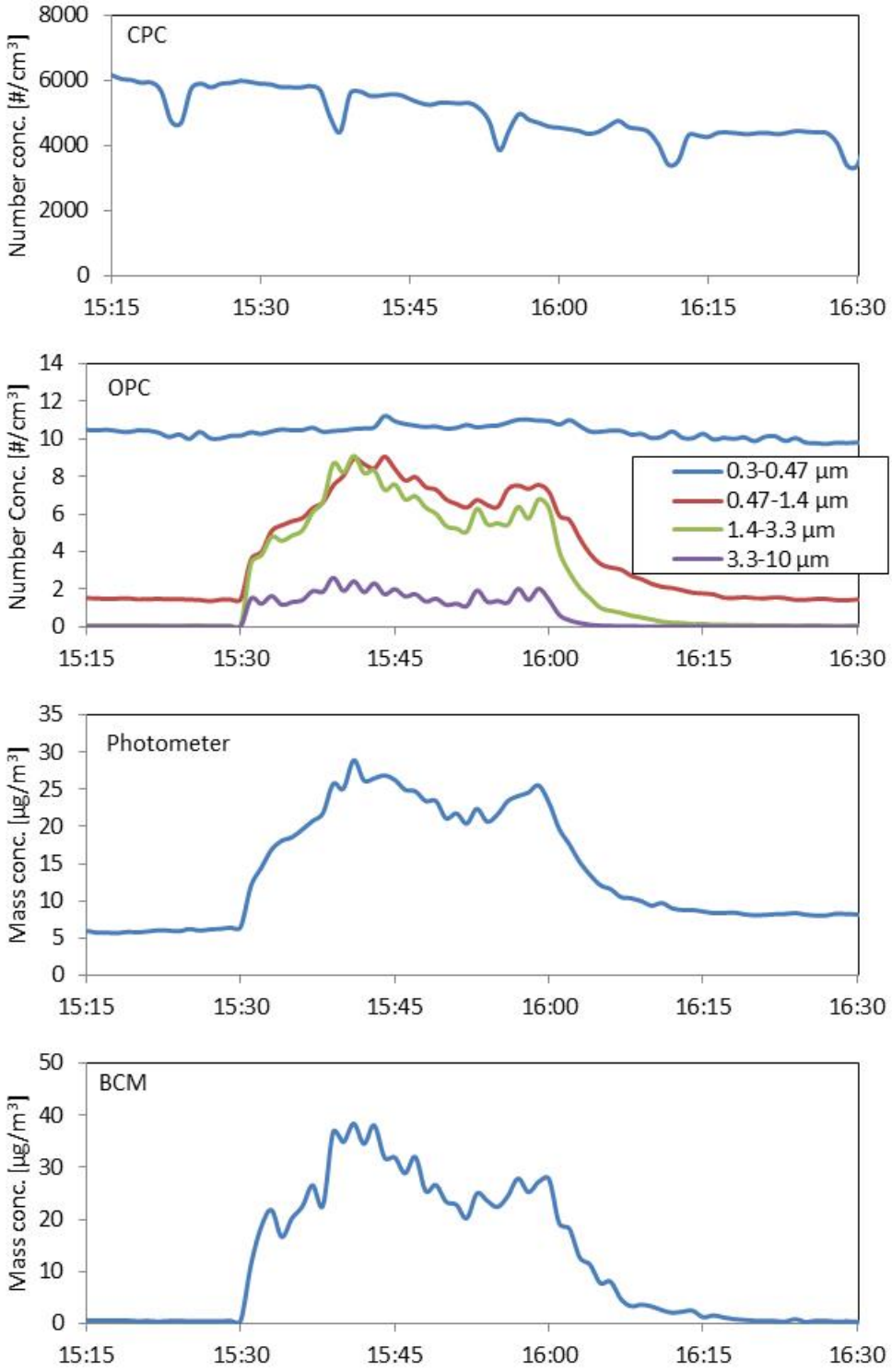

Figure 3.9 Measurement of the CNT transfer task
Operation over 15：30–16：00

3.5 Measurement case for a working environment handling CNTs

The following measurements were taken in a pilot-scale plant where SWCNTs were synthesized, harvested, and packed (Ogura *et al.* 2013). Each of the processes took place automatically within an enclosure that had a local exhaust device. Regardless of the presence or absence of worker exposure, to check for emission, the following measurements were made both inside and outside the enclosure and at a control point several meters away (center of the room).

(a) Mass concentration of total particles

Aerosol particles were collected on a Teflon filter (pore diameter 2 μm, outer diameter 37 mm) using a filter holder with a downward vertical open face (effective sampling area 9.6 cm^2) at a flow rate of 10 L/min. The collected particle mass was then analyzed with an ultra-microbalance (SE2-F, Sartorius, Germany).

(b) EC concentration of total particles

Aerosol particles were collected on a quartz fiber filter (diameter 37 mm) using a filter holder with a downward vertical open face (effective sampling area 9.6 cm^2) at a flow rate of 3 L/min. The EC mass was then analyzed with a thermal carbon analysis instrument (CAA-202M-D, Sunset Laboratory Inc., USA).

(c) EC concentration of respirable particles

After large aerosol particles were removed with a cyclone (50% reduction of particles of aerodynamic diameter 4 μm), aerosol particles of sizes that can be inhaled and reach the lungs were collected on a quartz fiber filter at a flow rate of 2.75 L/min. The EC mass was then analyzed with a thermal carbon analysis instrument.

(d) Morphological observations using FE-SEM

Aerosol particles were collected on a polycarbonate filter prepared in advance with vapor-deposited platinum/palladium (Nuclepore membrane, pore diameter 80 nm, density of 6×10^8 pores/cm^2, diameter 25 mm) using a stainless steel filter holder (effective sampling area 3.7 cm^2) at a flow rate of 0.5 L/min. The existence and form of the CNTs were observed with a FE-SEM.

Tables 3.3, 3.4, and 3.5 summarize the results for (a), (b), and (c), respectively. For the EC concentration of total particles collected inside the enclosure during the harvesting and packing (Table 3.4), values can be seen that are below the determination limit but exceed the lower detection limit. The EC detection fraction in this sample with combustion temperature is shown in Fig. 3.10. In this figure, the results from simulated emission tests (refer to Fig. 3.2) for the same CNTs carried out in the laboratory are also shown. The EC detection fraction for the harvesting and packing process, which was high in the region of 700–850 °C, was similar to those for the simulated emission tests, and therefore, the detected EC in the sample for the harvesting and packing process was considered to correspond to the aerosolized CNTs. Apart from this sample, the concentrations were all less than the detection limit. The mass concentration of total particles (Table 3.3) was approximately less than 20 μg/m^3, and the EC concentration of total particles (Table 3.4)

and the EC concentration of respirable particles (Table 3.5) were approximately less than 2 μg/m^3.

For the morphological observations using FE-SEM, micron-sized particles that appeared to be agglomerated CNT particles were observed in a sample collected in the enclosure during the harvesting and packing processes (Fig. 3.11). In addition, no particles that appeared to be CNTs were observed for other locations and processes.

Table 3.3 (a) Mass concentration of total particles

Process, measurement location	Sampling time [min]	Flow rate [L/min]	Total flow [L]	Collected particle mass [μg]	Mass concentration of airborne particles [μg/m^3]
Synthesizing CNTs (inside enclosure)	69	10	683	<13	<19
Synthesizing CNTs (outside enclosure)	68	10	683	<13	<19
Harvesting and packing CNTs (inside enclosure)	132	10	1338	<13	<9.7
Harvesting and packing CNTs (outside enclosure)	132	10	1326	<13	<9.8
The center of the room	270	10	2706	<13	<4.8

< denotes values below the detection limit (three times the standard deviation of the variation in the blank sample).

Table 3.4 (b) EC concentration of total particles

Process, measurement location	Sampling time [min]	Flow rate [L/min]	Total flow [L]	Collected EC mass [μg]	Airborne EC concentration [μg/m^3]
Synthesizing CNTs (inside enclosure)	69	3.0	206	<0.42	<2.1
Synthesizing CNTs (outside enclosure)	68	3.0	206	<0.42	<2.1
Harvesting and packing CNTs (inside enclosure)	132	3.0	403	(0.84)	(2.1)
Harvesting and packing CNTs (outside enclosure)	132	3.0	400	<0.42	<1.1
The center of the room	270	3.0	770	<0.42	<0.55

< denotes values below the detection limit (three times the standard deviation of the variation in the blank sample), and the values in parentheses are above the detection limit but below the determination limit (10 times the standard deviation of the variation in the blank sample).

Table 3.5 (c) EC concentration of respirable particles

Process, measurement location	Sampling time [min]	Flow rate [L/min]	Total flow [L]	Collected EC mass [μg]	Airborne EC concentration [μg/m^3]
Synthesizing CNTs (inside enclosure)	69	2.75	188	<0.42	<2.3
Synthesizing CNTs (outside enclosure)	68	2.75	187	<0.42	<2.3
Harvesting and packing CNTs (inside enclosure)	132	2.75	366	<0.42	<1.2
Harvesting and packing CNTs (outside enclosure)	132	2.75	363	<0.42	<1.2
The center of the room	270	2.75	756	<0.42	<0.56

< denotes values below the detection limit (three times the standard deviation of the variation in the blank sample).

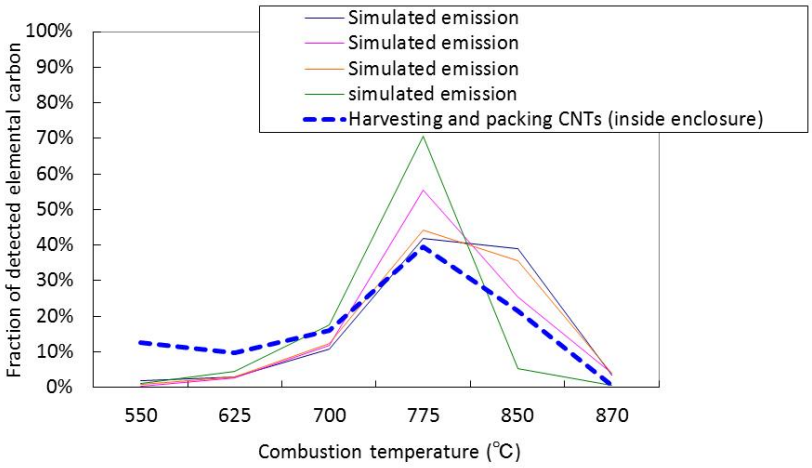

Figure 3.10 Fraction of elemental carbon (CNTs) detected with combustion temperature: Comparison between particles emitted in simulated tests and in harvesting and packing CNTs (inside enclosure)

For the harvesting and packing results, background concentration has been subtracted.

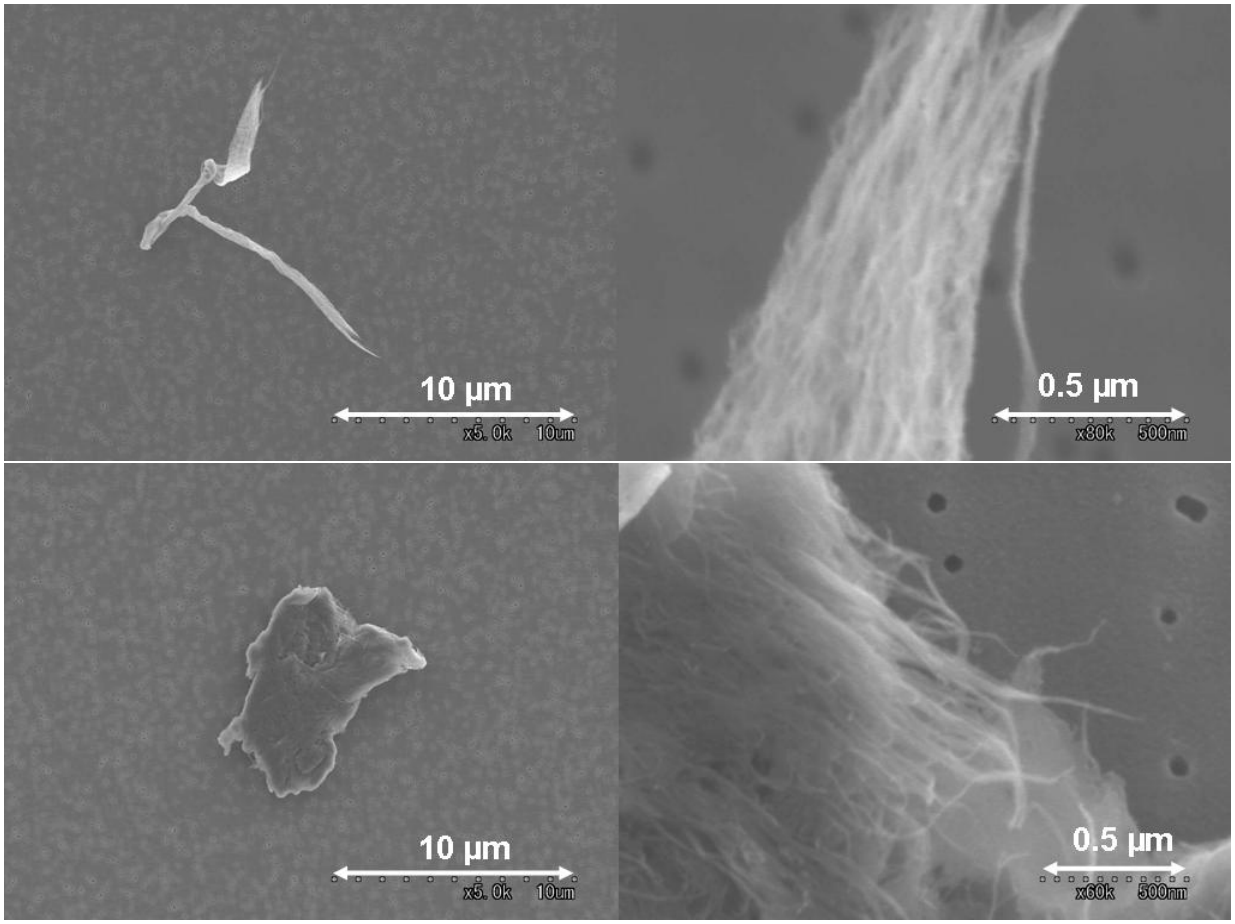

Figure 3.11 SEM micrographs of aerosol particles collected in the enclosure during the harvesting and packing processes

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