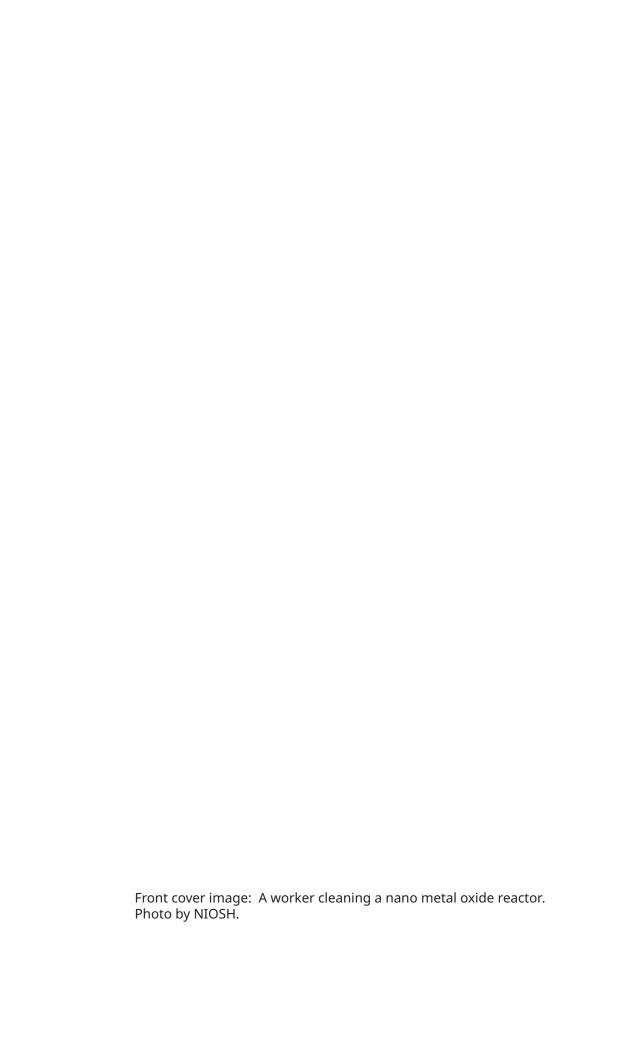
TECHNICAL REPORT

Occupational Exposure Sampling for Engineered Nanomaterials





Centers for Disease Control and Prevention National Institute for Occupational Safety and Health





Occupational Exposure Sampling for Engineered Nanomaterials

This document is in the public domain and may be freely copied or reprinted.

Disclaimer

Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention (CDC). In addition, citations to websites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these websites. All web addresses referenced in this document were accessible as of the publication date.

Get More Information

Find NIOSH products and get answers to workplace safety and health questions:

1-800-CDC-INFO (1-800-232-4636) | TTY: 1-888-232-6348

CDC/NIOSH INFO: cdc.gov/info | cdc.gov/niosh Monthly *NIOSH eNews*: cdc.gov/niosh/eNews

Suggested Citation

NIOSH [2022]. Occupational exposure sampling for engineered nanomaterials. Technical report. By Hodson L, Eastlake A. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2022-153.

DOI: https://doi.org/10.26616/NIOSHPUB2022153

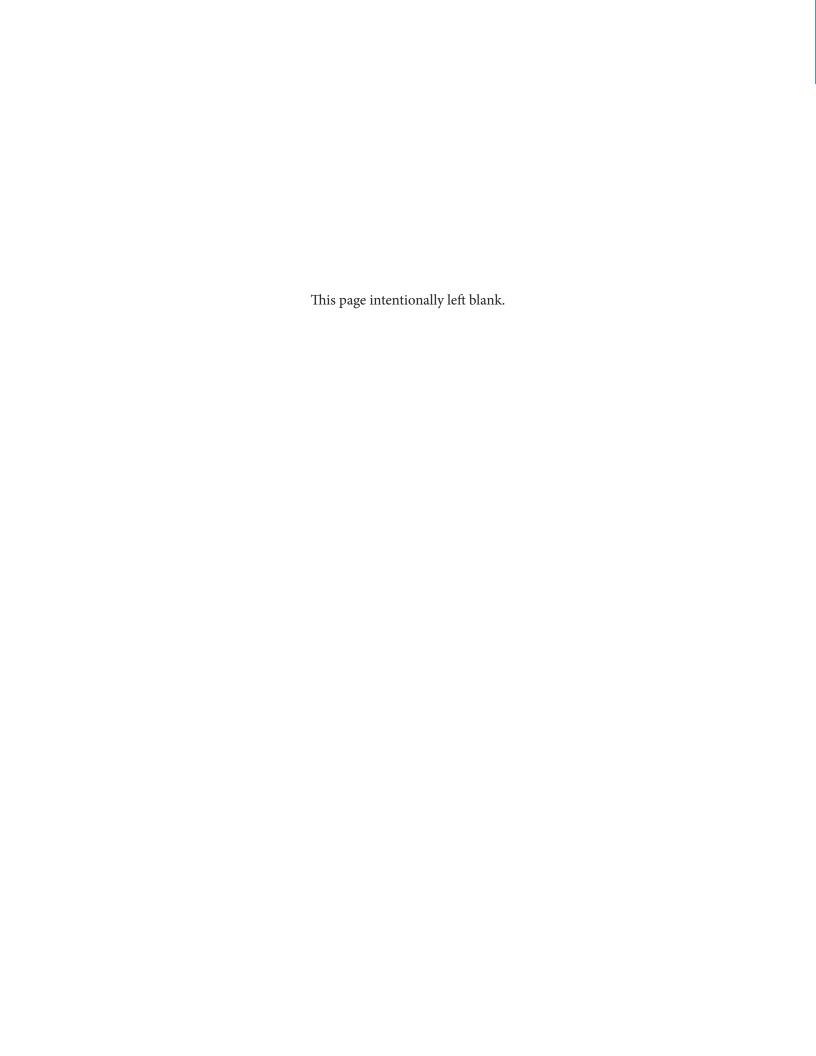
DHHS (NIOSH) Publication No. 2022-153

July 2022

Foreword

Increased engineered nanomaterial production, combined with widespread formulation and incorporation into nanomaterial enabled products, has increased the likelihood of occupational exposure. A key component in managing the occupational risk is exposure assessment. The National Institute for Occupational Safety and Health (NIOSH) developed guidance for workplace sampling for three engineered nanomaterials: carbon nanotubes and nanofibers, silver, and titanium dioxide, each of which have an elemental mass-based NIOSH Recommended Exposure Limit (REL). In addition, NIOSH developed a practical approach to exposure sampling for other engineered nanomaterials that do not have exposure limits. Occupational health and safety professionals have expressed a need for one document that explains all of the available nanomaterial sampling techniques, and this document provides a summary of the different sampling techniques. These techniques can be used to identify and assess potential occupational exposures to nanomaterials and to evaluate process emissions and engineering controls.

John Howard, M.D.
Director, National Institute for Occupational
Safety and Health
Centers for Disease Control and Prevention



Contents

Foreword	iii
Abbreviations	V
Acknowledgements	vi
Background	1
Health Effects	1
Recommendations	1
Exposure Monitoring Program	1
Carbon Nanotubes and Nanofibers (CNTs and CNFs)	2
Silver	5
Titanium Dioxide	7
Other ENMs: Use of the Nanomaterial Exposure Assessment Technique \dots	8
Optional Sampling Methods	11
Conclusions	14
References	14

Abbreviations

Ag silver

CIB current intelligence bulletin

CNF carbon nanofiber
CNT carbon nanotube

DRI direct reading instrument ENM engineered nanomaterial

HVAC heating, ventilation, and air conditioning

ICP-AES inductively coupled plasma atomic emission spectroscopy

NEAT 2.0 nanomaterial exposure assessment technique 2.0

MCE mixed cellulose ester

nm nanometer

NMAM NIOSH Manual of Analytical Methods NRD nanoparticle respiratory deposition

PBZ personal breathing zone

PENS personal nanoparticle sampler PPE personal protective equipment

PVC polyvinyl chloride

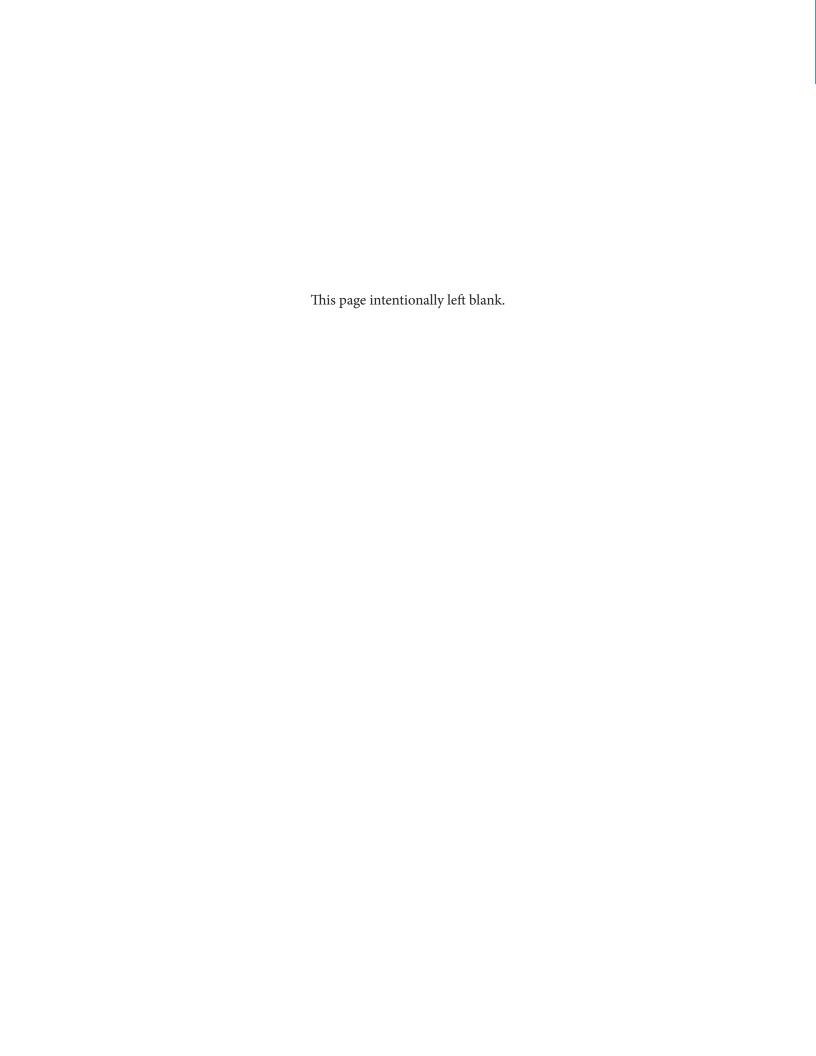
REL recommended exposure limit
TEM transmission electron microscope

TiO, titanium dioxide

TWA time-weighted average

Acknowledgements

The authors gratefully acknowledge the contributions of the following NIOSH personnel who assisted with the technical content and review of the document, including Matt Dahm PhD, Kevin L. Dunn MS, Kevin H. Dunn ScD, Charles Geraci PhD (retired), Eric Glassford MS, Eileen Kuempel PhD, Jenny Roberts PhD, Aleksandr Stefaniak PhD, Jay Vietas PhD, and Chen Wang PhD. External reviewers included David Abrams MSPH, ARS Environmental Health Inc.; John Baker MS, MBA, BSI EHS Services and Solutions (retired); Peter Raynor PhD, University of Minnesota; Keith Rickabaugh BS, MBA, R.J. Lee Group; Kevin Sheffield PhD, Phillips 66; and Candace Tsai PhD, University of California at Los Angeles.



Background

Engineered nanomaterial (ENM) is a classification for a diverse group of materials that have at least one dimension in the size range of 100 nanometer (nm) or less. Increased ENM production, combined with widespread formulation and incorporation into ENM-enabled products, has increased the likelihood of occupational exposure. Considering that some ENMs have enhanced toxicological concerns relative to their larger microscale material forms, there is a clear need to develop, implement, and apply a suitable strategy for occupational risk assessment and management [NIOSH 2011, 2013, 2021]. A key component of this strategy is exposure assessment. Unfortunately, a single instrument or analytical technique cannot always assess occupational exposure due to the variety of ENMs. Therefore, NIOSH recommends using a combination of measurement techniques and instruments to collect data to characterize process emissions and potential occupational exposures.

Health Effects

Studies in animals and cell systems show that some ENMs are more toxic than the microscale form of the same substance at equivalent mass doses. Based on high volume use and available toxicological information of three types of ENMs, NIOSH has developed recommended exposure limits (RELs) for airborne carbon nanotubes and nanofibers (CNTs and CNFs) [NIOSH 2013], silver (Ag) [NIOSH 2021], and titanium dioxide (TiO₂) [NIOSH 2011]. Studies in rats and mice show that CNTs and CNFs can pose a respiratory hazard due to pulmonary inflammation and rapidly developing, persistent fibrosis [NIOSH 2013; Wang et al. 2016]. Occupational exposure to CNTs and CNFs is associated with biomarkers of early effect for fibrosis, inflammation, oxidative stress, and cardiovascular responses in workers [Beard et al. 2018]. Silver nanoparticle inhalation exposure in rats for 90 days caused decreased lung function, inflamed lung tissue, and histopathological (microscopic tissue) changes in the liver and kidney [NIOSH 2021]. Studies of TiO₂ nanomaterials in rats found lung cancer after long-term inhalation exposures and non-cancerous effects (pulmonary inflammation, oxidative stress) after shorter exposures [Baranowska-Wójcik et al. 2020; NIOSH 2011].

Recommendations

Exposure Monitoring Program*

Safety and health professionals should incorporate ENMs into the existing exposure monitoring program with appropriate adjustments to ensure that worker exposures to ENMs are maintained below the RELs and to minimize exposures for ENMs without a

NIOSH recognizes contact through the skin, eating, or drinking as relevant pathways. This document focuses on exposure from breathing the material in because this is the only pathway for which RELs are available.

REL [NIOSH 2011, 2013, 2021]. Aspects of the program should include the following:

- 1. Identify sources of potential ENM exposures
- 2. Establish similar exposure groups by area or job tasks where workers may be exposed
- 3. Characterize exposures of all potentially exposed workers, and
- 4. Assess the effectiveness of engineering controls, work practices, personal protective equipment (PPE), training, and other factors used to reduce or eliminate potential exposures.

Exposure monitoring should include these elements:

- Develop an exposure assessment strategy. The details of the strategy will depend on several factors, including the number of workers potentially exposed to ENMs and the day-to-day and worker-to-worker variability in airborne concentrations. Because there is no "best" exposure measurement strategy that can be applied to all workplaces, multi-shift random sampling of workers (or all workers, if the exposed workforce is small) may be necessary to have an accurate assessment of worker airborne exposure concentration [NIOSH 2013].
- Identify areas and tasks that are more likely to emit ENMs, such as handling dry
 powders, or sonication of liquids [Dahm et al. 2018; Johnson et al. 2010]. The use
 of direct reading instruments may assist with identifying these work areas.
- Collect personal breathing zone (PBZ) samples for the worker's full shift to determine adherence to the applicable REL. Collect two paired side-by-side filter-based samples—one for elemental mass-based analysis, and one for ENM identification using electron microscopy. PBZ samples are also collected for samples without a REL to identify exposure potentials. Note that an ENM mass-based sample analysis may be below the detection limit of the method, and electron microscopy may be necessary to identify if there are ENMs.
- Collect area samples using filter-based samples at indoor locations both in near
 proximity and removed from the use of the ENM of interest to determine product migration and the extent of any cross contamination (from production to
 non-production work areas) from work practices or improperly designed HVAC or
 other ventilation systems.
- Use task-specific short-term PBZ and area sampling to identify those tasks that are more likely to emit ENMs.
- Consult with the analytical laboratory to evaluate detection limits and sample time/volumes to achieve a sensitive enough measurement.
- Submit media blanks, field blanks, and bulk materials, in addition to the samples collected, as required by the analytical laboratory.

Carbon Nanotubes and Nanofibers (CNTs and CNFs)

NIOSH derived a REL of 1 microgram per cubic meter ($\mu g/m^3$) for CNTs/CNFs (with two dimensions < 100 nm) as measured by elemental carbon as a respirable mass 8-hour

time-weighted average (TWA) concentration [NIOSH 2013]. Personal exposure concentrations to elemental carbon as a proxy for CNT and CNF, can be determined by NIOSH Method 5040 [NIOSH 2003, 2004, 2013].

Use the following approach for paired filter-based sampling (Figure 1) [NIOSH 2013]:

- Sample collection:
 - O Collect paired filter air samples in the worker's PBZ near process locations with at least one at a background location as described below. Each sampling pair should include one air sampling cassette that contains a quartz fiber filter attached to a respirable cyclone, and one cassette containing a mixed cellulose ester or polycarbonate filter, with each cassette connected to a separate sampling pump. Consider additional sampling for the inhalable fraction of elemental carbon using a quartz fiber filter in the PBZ and background as some CNT/CNF materials may agglomerate to particle sizes beyond the respirable size fraction [Dahm et al. 2018].
- Elemental mass-based analysis—carbon:
 - o Analyze the quartz fiber filter for elemental carbon using NIOSH Method 5040.
- Nanomaterial identification—electron microscopy:
 - O Use elemental microscopy techniques such as transmission electron microscopy, high resolution scanning electron microscopy, or scanning transmission electron microscopy analysis for CNT and CNF identification. If possible, elemental microscopy analysis should also be performed on bulk samples to characterize the characteristics of the ENM to apply to air samples.
 - O Consider analyzing the mixed cellulose ester filters as described in Chapter CN of the NIOSH Manual of Analytical Methods (NMAM), 5th edition [NIOSH 2016]. Elemental microscopy visualization can also identify whether there are particles, agglomerates, or whether the CNT or CNF is embedded within a matrix.
 - O Determine the elemental composition of particles and morphological features (e.g., size, shape, and agglomeration state) consistent with CNT and CNF by using an energy dispersive X-ray spectrometry system attached to the transmission electron microscope.
- Background correction of elemental carbon:
 - Ocllect background respirable and, if determined necessary, inhalable samples for elemental carbon determination. Use a quartz fiber filter in a sampling cassette attached to a respirable cyclone and sampling pump at indoor locations where exposure to CNT or CNF is unlikely. For example, a location removed from the use of CNTs or CNFs and in an area with a different ventilation system. Also consider collecting an outdoor background sample as some areas, like those near major public roads, may have higher outdoor contributors to elemental carbon than indoor background samples. This collection strategy considers the potential for incidental elemental carbon contributions, such as from internal combustion engines or wildfires.

- O Subtract the elemental carbon concentrations determined from background samples from the PBZ sample results to determine whether worker exposures exceed the REL. Initially, more samples may be required to characterize the workplace thoroughly. This initial assessment will help refine the sampling approach and determine whether elemental carbon interference is an issue. Careful consideration of environmental background is essential. For example, outdoor elemental carbon may sometimes be higher or lower than indoor background depending on the facility's air handling system.
- If the PBZ sample results are above the REL, consider following methods outlined in the hierarchy of controls (elimination, substitution, engineering controls, administrative controls and personal protective equipment), until exposures are controlled below the REL.
- Once the exposure is well characterized and controlled below the REL, use quartz
 fiber filter samples collected with the chosen size-selective sampler and analyzed
 with NIOSH Method 5040 to periodically monitor elemental carbon exposure.
 Reassess exposures if the production increases or the process changes.

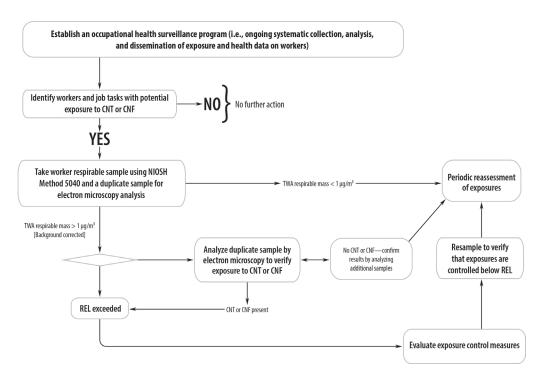


Figure 1. Exposure measurement strategy for CNT and CNF [NIOSH 2013].

Silver

NIOSH derived a REL for silver nanoparticles (all three primary particle size dimensions < 100 nm) of 0.9 $\mu g/m^3$ as a respirable 8-hour TWA concentration [NIOSH 2021]. NIOSH continues to recommend a REL of 10 $\mu g/m^3$ as an 8-hour TWA for total silver (metal dust, fume, and soluble compounds).

Use the following approach for paired filter-based sampling (Figure 2) [NIOSH 2021]:

- Sample collection:
 - Ocllect a set of two filter air samples in the worker's PBZ and a set in at least one location outside of the production area. Use 37-millimeter (mm) diameter mixed cellulose ester filters in sampling cassettes attached to respirable cyclones with each connected to a sample pump calibrated at the cyclone specified flow rate. A polycarbonate filter could also be used instead of a mixed cellulose ester filter for a sample collected for elemental microscopy analysis if scanning electron microscopy analysis techniques are used.
- Elemental mass-based analysis—silver:
 - o Analyze one of the mixed cellulose ester PBZ filters from the set by NIOSH Method 7300 utilizing Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to determine the mass of silver present, accounting for wall deposits as described by NIOSH Method 7306 and Chapter 0 [NIOSH 1994, 2016]. Results below 0.9 $\mu g/m^3$ will affirm that exposures are below the REL for silver nanoparticles.
- Nanomaterial identification—electron microscopy:
 - O If the mass-based result is at or above 0.9 $\mu g/m^3$, further characterize the duplicate sample with electron microscopy equipped with X-ray energy dispersive spectroscopy. Determine the silver particle size since there are different RELs depending upon the particle size (0.9 $\mu g/m^3$ for ultrafine < 100 nm and 10 $\mu g/m^3$ for total silver). This analysis can identify particles and agglomerates of primary particles of 100 nm or less, so the mass fraction that the silver nanomaterial REL applies to can be determined. For example, if the mass-based result is 9 $\mu g/m^3$, and the percent of < 100 nm silver particles determined by electron microscopy is only 5%, the exposure to silver ENM would be 0.45 $\mu g/m^3$ and the REL would not be exceeded.
- Collect area air samples for silver at indoor locations removed from the use of silver to determine whether the source is controlled or the extent of any cross contamination from the work practices. These area samples are not considered "background" samples; they should not be subtracted from the silver PBZ sample results to determine whether worker exposures exceeded the REL.
- If PBZ sample results are above the REL, consider following methods outlined in the hierarchy of controls until exposures are controlled below the REL.
- Once the exposure is well characterized and controlled below the REL, periodically
 monitor exposure. Use mixed cellulose ester filter samples collected with the
 respirable cyclone and analyzed with NIOSH Method 7300. Reassess exposures if
 the production increases or the process changes.

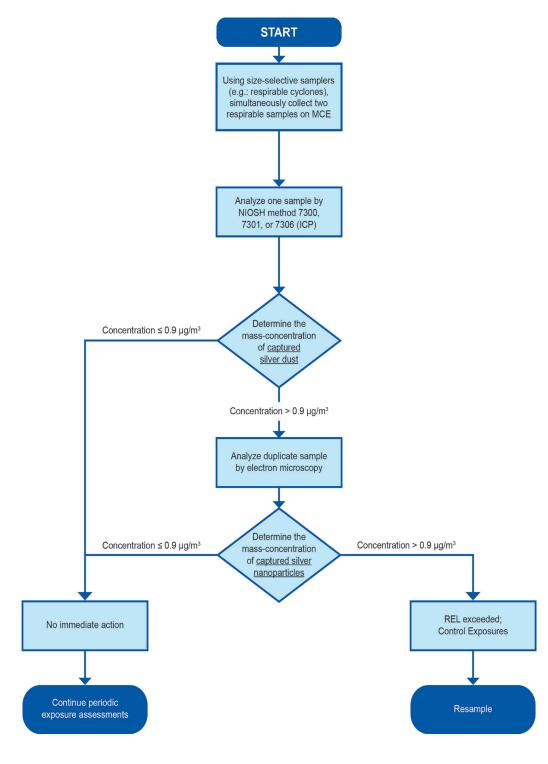


Figure 2. Exposure measurement strategy for silver nanoparticles [NIOSH 2021].

Titanium Dioxide

NIOSH derived RELs of 2.4 milligrams per cubic meter (mg/m³) for fine ${\rm TiO}_2$ (> 100 nm) and 0.3 mg/m³ for ultrafine (all three primary particle size dimensions < 100 nm) ${\rm TiO}_2$, as TWA concentrations for up to 10 hours per day during a 40-hour work week [NIOSH 2011].

Use the following approach for paired filter-based sampling (Figure 3) [NIOSH 2011]:

- Sample collection:
 - Ocllect a set of two filter-based air samples in the worker's PBZ and a set of filter samples in an area location using a 37-mm cassette containing a hydrophobic polyvinyl chloride filter in one cassette and a mixed cellulose ester filter in the second cassette. Sets of samples in both locations should be attached to respirable cyclones and sample pumps calibrated at the cyclone specified flow rate.
- Mass-based analysis—TiO₃:
 - O Analyze the polyvinyl chloride filter for respirable mass. If the air concentration result is less than 0.3 mg/m³, no further action is required. Sampler wall losses can be addressed following NMAM Chapter O [NIOSH 2016].
 - O If the total mass is ≥ 0.3 mg/m³, analyze the same polyvinyl chloride filter for elemental titanium by NIOSH Method 7300 [NIOSH 1994].

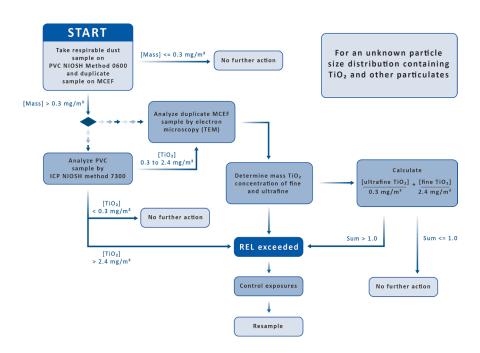


Figure 3. Exposure measurement strategy for titanium dioxide (TiO₂) [NIOSH 2011].

Nanomaterial identification—electron microscopy:

- O If the exposure concentration of elemental titanium by mass ≥ 0.3 mg/m³ using NIOSH Method 7300, characterize the mixed cellulose ester filter using electron microscopy. This is necessary to determine the particle size since there are different RELs depending upon the particle size. When feasible, determine the percentage of fine (> 0.1 micrometer [µm]) and ultrafine (< 0.1 µm) TiO₂ based on the measurement of "primary" particles (including agglomerates comprised of primary particles).
- O The primary particle size of the bulk powder can also be used as a starting point to determine whether to apply the REL for fine or ultrafine TiO₂.
- Collect area air samples for TiO₂ at indoor locations removed from the use of TiO₂ to determine whether the source is controlled or the extent of any cross contamination from the work practices. These area samples are not considered "background" samples; they should not be subtracted from the PBZ sample results to determine whether worker exposures exceeded the REL.
- If PBZ sample results are above the REL, consider following methods outlined in the hierarchy of controls until exposures are controlled below the REL.
- Once the exposure is well characterized and controlled below the REL, use polyvinyl chloride filter samples collected with the respirable cyclone and analyzed with NIOSH Method 7300 to periodically monitor exposure. Reassess exposures if the production increases or the process changes.

Other ENMs: Use of the Nanomaterial Exposure Assessment Technique

When there is no available REL with described sampling techniques, the Nanomaterial Exposure Assessment Technique (NEAT 2.0) can help to quantify exposures to the ENM of interest [Eastlake et al. 2016]. NEAT 2.0 includes paired filter-based sampling in concert with real-time direct reading instruments (DRIs), including particle counters with data logging capabilities.

This strategy requires the collection of a pair of full-shift, filter-based air samples from the worker's PBZ. If there is interest in identifying task-specific exposure information, collect additional samples in the worker's PBZ for the duration of that specific task. Evaluate area airborne particle measurements using DRIs such as a condensation particle counter, an optical particle counter, or a photometer to identify potential emission sources.

- Sample collection:
 - O Collect filter-based samples at the desired aerosol size fraction using a size selective cyclone that meets the volume and loading requirements specified by the analysis method, in the worker's PBZ and in area locations close to process areas and in areas removed from the process. The type of filter media used for the elemental analysis will depend on the chemical composition of the ENM of interest (for example, mixed cellulose ester for metals and either mixed cellulose ester or polycarbonate for electron microscopy) as specified in the

NMAM [NIOSH 2016]. Consult with an analytical lab before collecting samples to determine if an appropriate analysis method exists. Flow rates and the use of size selective samplers will depend on methodological needs. In some cases, an additional filter-based sample can be collected at a different particle size fraction, such as one sample collected at the inhalable fraction and one sample collected at the respirable fraction. This paired sampling approach enables better understanding of the contribution of particle agglomeration and exposure to larger particles in the analysis of worker exposures.

- Elemental mass-based analysis:
 - O Conduct elemental analysis of the ENM of interest on one of the filters from each sampling set. Since occupational exposure criteria do not exist for most ENMs, it is not possible to compare the PBZ measurements with corresponding occupational exposure criteria for the parent compound. Comparisons to the parent compound are inappropriate because many of the ENMs studied to date have more significant toxicological concerns than the larger forms of the element(s) from which they are derived [NIOSH 2011, 2013, 2021].
- Nanomaterial identification—electron microscopy:
 - O Analyze the second filter sample from the set by electron microscopy for visualization of size and determination of elemental composition of particles to confirm the presence or absence of the ENM of interest. The use of electron microscopy-based methods also enables the examination of various particle attributes (such as physical size, morphology, and composition) that helps distinguish the ENM of interest from incidental nanomaterials [Peters et al. 2008]. In addition, electron microscopy methods can identify the presence of an ENM of interest even when its mass concentration is below the level of detection of the elemental analysis. Consult with your microscopist to determine the best filter type and analytical technique for the ENM of interest. If possible, provide a sample of the bulk ENM to the analytical laboratory.
 - O Consideration should be given to use of nanoparticle sampling methods that deposit particles directly onto microscopy grids in addition to collection on a filter. See the section on Optional Sampling Methods below.
- Collect area filter-based air samples at indoor locations both in near proximity and removed from the use of the ENM to determine whether the source is controlled or the extent of any cross contamination from the work practices. These samples can also be used to identify low level/trace contamination in nonoperational areas. These area samples are not considered "background" samples; they should not be subtracted from the PBZ sample results to determine worker exposures.
- If the worker is expected to wear multiple pumps (such as two for a task-based set and two for a full-shift sampling set), consider using a sampling vest to hold the sampling equipment. This will disturb the worker less and distribute the weight of the pumps more evenly (Figure 4).

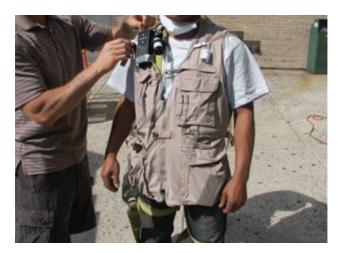


Figure 4. Exposure measurement sampling for ENMs using NEAT 2.0. This worker has two filter-based personal breathing zone samples in addition to a thermophoretic sampler, which was being evaluated (Photo by NIOSH).

Direct reading instruments:

- O Use DRIs for area air sampling to help find the tasks with the greatest emission and exposure potential to identify workers who should be monitored with PBZ filter-based sampling. The DRIs can also supplement the time-integrated filter samples (including those collected to determine compliance to nano RELs), by logging changes in particle counts or mass over time and correlating to events. DRIs such as condensation and optical particle counters, and photometers can determine variations in number concentration, mass concentration, and/or approximate size range of particles. NEAT 2.0 recommends the use of a suite of DRIs together at the same locations where filter-based area samples are collected because not all instruments can determine the presence of all size ranges. These instruments should be used in data-log mode. If accurate field notes are taken detailing worker processes and the timing of tasks throughout the day, the data obtained from the stationary DRIs can provide insight into specific worker activities or tasks that contribute to an increase or decrease in particle concentrations or counts. Ensure that the data/time settings of each of the DRIs intended to be used are simultaneously synchronized to ease the data comparison task.
- O While NIOSH often uses an array of different DRIs to collect information on particles of different size ranges and agglomeration states, this may not always be necessary. For instance, one type of DRI could be used to conduct control technology evaluations, like a condensation particle counter that counts particles in the size range of nominally 10–1,000 nm. NIOSH includes additional DRIs to fully understand whether the nanomaterial of interest is also present in the larger particle sizes or agglomerates. NIOSH recommends the use of DRIs primarily to verify that engineering controls are functioning properly and to qualitatively identify tasks or areas of potential exposure. DRIs lack the specificity required for a quantitative exposure assessment but can help identify and evaluate particle concentration trends.

Use all three sampling methods (elemental mass-based analysis, electron microscopy identification, and direct-reading instruments) for a complete exposure assessment (Figure 5).



Figure 5. Area sampling shown in the figure includes three real-time data logging particle counters (one condensation particle counter and two optical particle counters), two 25-mm open-face filter cassettes, and two thermophoretic samplers (Photo by NIOSH).

Optional Sampling Methods

Personal samplers for ENMs are continually being developed, and several are listed in Table 1. In general, these instruments consist of a particle size-selective inlet, a sampling substrate like a filter cassette/net/grid, and a sampling pump [Eastlake et al. 2020; Iavicoli et al. 2018; Tsai et al. 2018]. Substrates from personal sampling devices can be removed and characterized using sophisticated analytical techniques, such as inductively coupled plasma mass spectrometry (ICP-MS); electron microscopic with chemical detectors, or Raman spectroscopy analyses, to obtain information (e.g., mass, chemical composition, size, and shape). These techniques can also be used for area sampling and provide a wealth of information about the ENM of interest. Nanoparticle sampling methods that deposit particles directly onto electron microscopy grids show great promise [Asbach et al. 2017; Iavicoli et al. 2018; NanoIndEx Project 2016; Tsai et al. 2018]. These personal samplers could also be used for area sampling.

Table 1. Personal measurement methods and brief descriptions

Measurement Method	Manufacturer	Description
Electrostatic Precipitator [Miller et al. 2010]	ESPNano; Spokane, WA	Eliminates the use of filter- based sampling by collecting directly onto an electron microscopy grid using a charge differential. Analyzed in a laboratory using electron microscopy.
Identifier C1 (carbon nanotubes & graphene), S1 (silica), or N1 (nanocellulose) [Bieri and Cattaneo 2016]	StatPeel; Switzerland	A product composed of several individual employee badge sensors and an integrated bench-top optical reader. The badges are used to monitor and record exposure to nanomaterials. Analysis is performed on site by Raman spectroscopy in the integrated optical reader or can be submitted for laboratory analysis.
MPS Mini-Particle Sampler [R'mili et al. 2013]	Ecomesure; Janvry, France	Uses a transmission electron microscopy grid as a filter to collect particles with subsequent identification and chemical analysis. Analyzed in a laboratory using electron microscopy.
Nanobadge [Iavicoli et al. 2018]	Nano Inspect, Alcen Group; Paris, France and French Alternative Energies and Atomic Energy Commission CEA, Grenoble, France	Product collects particles directly onto a polycarbonate track-etched membrane or quartz filter. Analyzed in a laboratory using X-ray fluorescence spectroscopy or scanning electron microscopy.
Nanoparticle Respiratory Deposition Sampler (NRD) [Cena et al. 2011]	Zefon International; Ocala, FL	Sampler designed to mimic the deposition of nanoparticles (of less than 300 nanometers) in the human respiratory system. Analyzed in a laboratory using specialized NRD protocol.

Measurement Method	Manufacturer	Description
Partector TEM [Fierz et al. 2015]	Naneos Particle Solutions GmbH; Windisch, Switzerland	Eliminates the use of filter- based sampling by collecting directly onto an electron microscopy grid. Analyzed in a laboratory using electron microscopy.
PENS Personal Nanoparticle Sampler Electrostatic Precipitator [Tsai et al. 2012]	Institute of Environmental Engineering, National Chiao Tung University; Taiwan	The PENS consists of a respirable cyclone, a micro-orifice impactor and a rotating, silicone oil-coated Teflon filter substrate. Analyzed in a laboratory for mass.
Personal Sampling System, Personengetragenes Gefahrstoff- Probenahmesystem (PGP) [Asbach et al. 2015]	GSA Messgerätebau GmbH; Ratingen, Germany	Product collects particles directly onto a gold-coated etch membrane filter. Analyzed in a laboratory using scanning electron microscopy.
TDS-Diffusion sampler [Tsai and Theisen 2018]	Tsai Lab at University of California; Los Angeles, CA	A 3D-print sampling cassette connecting to personal sampling pump, collects size-selective nanoparticles and respirable particles onto a transmission electron microscopy grid and polycarbonate membrane filter. Analyzed in a laboratory using electron microscopy.
Thermophoretic Sampler [Leith et al. 2014]	RJ Lee Group; Monroeville, PA	Eliminates the use of filter- based sampling by collecting directly onto an electron microscopy grid using a temperature differential. Analyzed in a laboratory using electron microscopy.

Incorporating surface wipe or bulk dust sampling can also be useful to identify ENM migration throughout production areas or contamination of nonproduction work areas of the facility. Although there are no surface contamination standards for ENMs, some workplaces have developed internal standards for surface contamination. For example, Brookhaven National Laboratory developed guidance for surface contamination of some non-nano elements [BNL 2017]. Periodic surface sampling can identify if there is material transfer out of working or production areas, and helps to ensure that risk management practices operate effectively by keeping ENMs from spreading within production areas or into surrounding nonproduction areas.

Conclusions

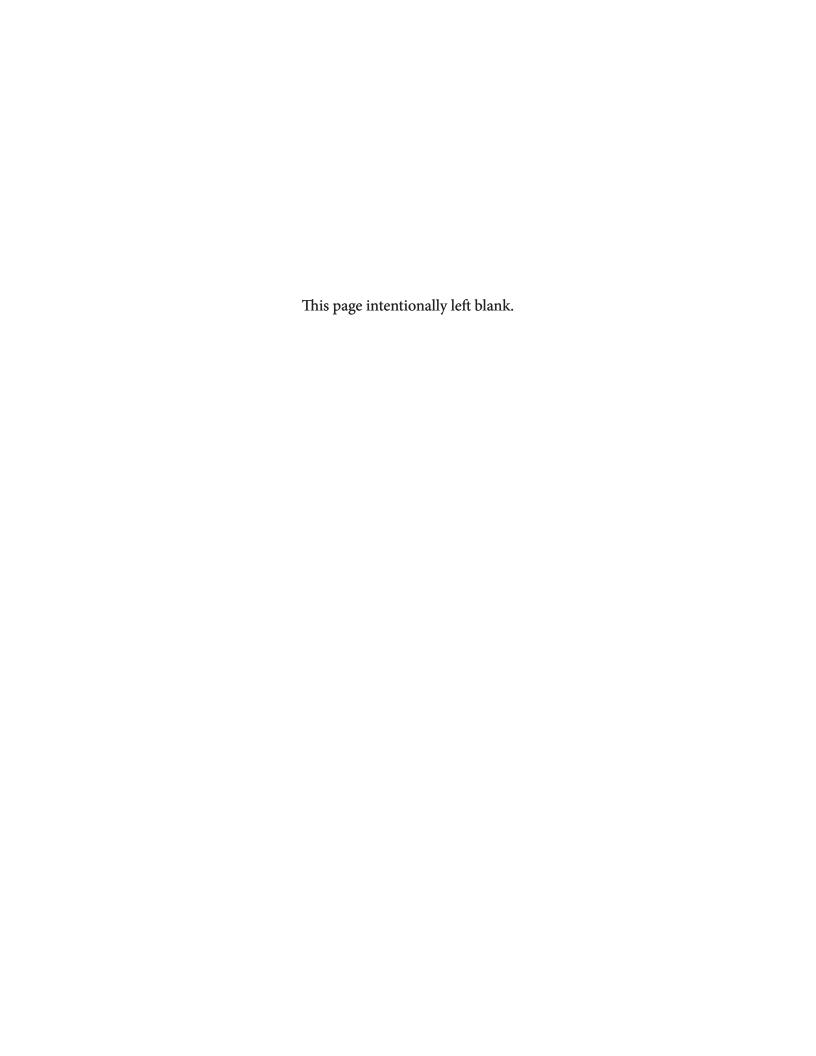
A comprehensive exposure assessment evaluation for ENMs collects information that can be used to (1) identify sources of potential ENM exposures, (2) establish similar exposure groups by area or job tasks, (3) characterize exposures of all potentially exposed workers, and (4) assess the effectiveness of engineering controls, work practices, PPE, training, and other factors used in reducing exposures. Using a combination of the techniques described above can provide an in-depth characterization of potential occupational exposure to ENMs. This information is then available for incorporation into risk management strategies to minimize worker exposure to ENMs and confirm ongoing control of risk.

References

- Asbach C, Alexander C, Clavaguera S, Dahmann D, Dozol H, Faure B, Fierz M, Fontana L, Iavicoli I, Kaminski H, MacCalman L, Meyer-Plath A, Simonow B, van Tongeren M, Todea AM [2017]. Review of measurement techniques and methods for assessing personal exposure to airborne nanomaterials in workplaces. Sci Total Environ 603–604:793–806, https://doi.org/10.1016/j.scitotenv.2017.03.049.
- Asbach C, Clavaguera S, Todea AM [2015]. Measurement methods for nanoparticles in indoor and outdoor air. Viana M, ed. In: Indoor and outdoor nanoparticles. The handbook of environmental chemistry. Vol. 48. Cham, Switzerland: Springer.
- Baranowska-Wójcik E, Szwajgier D, Oleszczuk P, Winiarska-Mieczan A [2020]. Effects of titanium dioxide nanoparticles exposure on human health—a review. Biol Trace Elem Res 193:118–129, https://doi.org/10.1007/s12011-019-01706-6.
- Beard JD, Erdely A, Dahm MM, de Perio MA, Birch ME, Evans DE, Fernback JE, Eye T, Kodali V, Mercer RR, Bertke SJ, Schubauer-Berigan MK [2018]. Carbon nanotube and nanofiber exposure and sputum and blood biomarkers of early effect among U.S. workers. Environ Int 116:214–228, https://doi.org/10.1016/j.envint.2018.04.004.
- Bieri R, Cattaneo S [2016]. Device for measuring the exposure to small particles, in particular nano tubes. U.S. Patent 10,739,268. Washington, DC: United States Patent and Trademark Office, https://www.uspto.gov/.
- BNL [2017]. Standard operating procedure IH75190. Surface wipe sampling for metals. Upton, NY: Brookhaven National Laboratory (BNL), https://www.bnl.gov/esh/shsd/sop/pdf/ih_sops/ih75190.pdf.
- Cena LG, Anthony TR, Peters TM [2011]. A personal nanoparticle respiratory deposition (NRD) sampler. Environ Sci Technol 45(15):6483–6490, https://doi.org/10.1021/es201379a.
- Dahm MM, Schubauer-Berigan MK, Evans DE, Birch ME, Bertke S, Beard JD, Erdely A, Fernback JE, Mercer RR, Grinshpun SA [2018]. Exposure assessments for a cross-sectional epidemiologic study of US carbon nanotube and nanofiber workers. Int J Hyg Environ Health 221(3):429–440, https://doi.org/10.1016/j.ijheh.2018.01.006.
- Eastlake AC, Beaucham C, Martinez KF, Dahm MM, Sparks C, Hodson LL, Geraci CL [2016]. Refinement of the nanoparticle emission assessment technique into the nanomaterial exposure assessment technique (NEAT 2.0). J Occup Environ Hyg 13(9):708–717, https://doi.org/10.1080/15459624.2016.1167278.
- Eastlake AC, Fontana L, Iavicoli I [2020]. Monitoring nanomaterials in the workplace. In: Otsuki T, Di Gioacchino M, Petrarca C, eds. Current topics in environmental health and preventive medicine. Allergy and immunotoxicology in occupational health—the next step. Singapore: Springer, https://doi.org/10.1007/978-981-15-4735-5_5.

- Fierz M, Meier D, Steigmeier P, Burtscher H [2015]. Miniature nanoparticle sensors for exposure measurement and TEM sampling. J Phys Conf Ser 617:012034, https://doi.org/10.1088/1742-6596/617/1/012034.
- Johnson DR, Methner MM, Kennedy AJ, Steevens JA [2010]. Potential for occupational exposure to engineered carbon-based nanomaterials in environmental laboratory studies. Environ Health Perspect 118(1):49–54, https://doi.org/10.1289/ehp.0901076.
- Iavicoli I, Fontana L, Pingue P, Todea AM, Asbach C [2018]. Assessment of occupational exposure to engineered nanomaterials in research laboratories using personal monitors. Sci Total Environ 627:689–702, https://doi.org/10.1016/j.scitotenv.2018.01.260.
- Leith D, Miller-Lionberg D, Casuccio G, Lersch T, Lentz H, Marchese A, Volckens J [2014]. Development of a transfer function for a personal, thermophoretic nanoparticle sampler. Aerosol Sci Technol 48(1):81–89, https://doi.org/10.1080/02786826.2013.861593.
- Miller A, Frey G, King G, Sunderman C [2010]. A handheld electrostatic precipitator for sampling airborne particles and nanoparticles. Aerosol Sci Technol 44(6):417–427, https://doi.org/10.1080/02786821003692063.
- NanoIndEx Project [2016]. Assessment of personal exposure to airborne nanomaterials—a guidance document. Bonn, Germany: Federal Ministry of Education and Research, https://nanopartikel.info/wp-content/uploads/2020/10/NanoIndEx-GuidanceDocument-2016.pdf.
- NIOSH [2021]. Health effects of occupational exposure to silver nanomaterials. By Kuempel E, Roberts JR, Roth G, Dunn KL, Zumwalde R, Drew N, Hubbs A, Trout D, Holdsworth G. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2021-112, https://doi.org/10.26616/NIOSHPUB2021112.
- NIOSH [2016]. NIOSH manual of analytical methods (NMAM). 5th ed. Ashley K, O'Conner PF, eds. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, https://www.cdc.gov/niosh/nmam/default.html.
- NIOSH [2013]. Occupational exposure to carbon nanotubes and nanofibers. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2013-145, https://www.cdc.gov/niosh/docs/2013-145/default.html.
- NIOSH [2011]. Occupational exposure to titanium dioxide. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 2011-160, https://www.cdc.gov/niosh/docs/2011-160/default.html.
- NIOSH [2004]. Monitoring of diesel particulate exhaust in the workplace. By Birch ME. Chapter Q. In: Schlecht PC, O'Connor PF, eds. NIOSH manual of analytical methods (NMAM). 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2003-154, https://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-q.pdf.
- NIOSH [2003]. NIOSH method 5040 update. By Birch ME. In: Schlecht PC, O'Connor PF, eds. NIOSH manual of analytical methods (NMAM). 4th ed., 3rd suppl. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2003-154, https://www.cdc.gov/niosh/docs/2003-154/pdfs/5040.pdf.
- NIOSH [1994]. NIOSH manual of analytical methods (NMAM). 4th ed. Cassinelli ME, O'Conner PF, eds. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 94-113.
- Peters TM, Elzey S, Johnson R, Park H, Grassian VH, Maher T, O'Shaughnessy P [2008]. Airborne monitoring to distinguish engineered nanomaterials from incidental particles

- for environmental health and safety. J Occup Environ Hyg *6*(2):73–81, https://doi.org/10.1080/15459620802590058.
- R'mili B, Le Bihan OLC, Dutouquet C, Aguerre-Charriol O, Frejanfon E [2013]. Particle sampling by TEM grid filtration. Aerosol Sci Tech 47(7), https://doi.org/10.1080/02786826.2013.789478.
- Tsai CJ, Liu CN, Hung SM, Chen SC, Uang SN, Cheng YS, Zhou Y [2012]. Novel active personal nanoparticle sampler for the exposure assessment of nanoparticles in workplaces. Environ Sci Technol 46(8):4546–4552, https://pubs.acs.org/doi/10.1021/es204580f.
- Tsai CSJ, Theisen D [2018]. A sampler designed for nanoparticles and respirable particles with direct analysis feature. J Nanopart Res 20:209, https://doi.org/10.1007/s11051-018-4307-2.
- Tsai CSJ, Castano A, Khattak J, Ellenbecker M [2018]. Nano particle collection by various sampling techniques for worker exposure assessment. Int J Occup Environ Hyg 105, https://www.gavinpublishers.com/article/view/nano-particle-collection-by-various-sampling-techniques-for-worker-exposure-assessment.
- Wang L, Davidson DC, Castranova V, Rojanasakul Y [2016]. Pulmonary effects of carbon nanomaterials. Biomedical applications and toxicology of carbon nanomaterials. Chen C, Wang H, eds. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, https://doi.org/10.1002/9783527692866.ch6.





Promoting productive workplaces through safety and health research

DHHS (NIOSH) Publication No. 2022-153

DOI: https://doi.org/10.26616/NIOSHPUB2022153