Evaluating nanoparticle emissions in the workplace: A description of the approach used by NIOSH and a summary of findings from 12 site visits

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ABSTRACT

NIOSH created a field team to assess potential workplace exposures to engineered nanoparticles. After exploratory field research efforts aimed at characterizing potential emissions and worker exposure using complex, not easily portable instrumentation, the field team subsequently developed a portable procedure that could be adopted by other health and safety professionals interested in determining potential releases of engineered nanoparticles from various processes. The nanoparticle emission assessment technique (NEAT) used by the NIOSH field team includes portable, direct-reading instrumentation (condensation and optical particle counters) supplemented by filter-based air samples (source-specific and personal breathing zone [PBZ]). This technique was used at 12 facilities to assess workplace emissions and potential worker exposures.

Keywords: emission assessment, measurement, identification.

1 INTRODUCTION

Health, safety, and environmental issues continue to be a high priority area to be addressed during the commercialization of nanomaterials or nanomaterial-enabled products [1]. Facilities engaged in the production or use of engineered nanomaterials, specifically nanoparticles, have expressed an interest in learning if their processes present any potential for worker exposure. To assist with answering this question, NIOSH created a nanotechnology field research team tasked with visiting facilities and collecting information about the potential for release of nanoparticles and worker exposure. The nanotechnology field research team quickly discovered that many of the sampling techniques and instruments available for measuring airborne nanoparticles vary in complexity and provide a variety of information for evaluating occupational exposures with respect to particle size, mass, surface area, number concentration and composition. Unfortunately, relatively few of the available techniques and instruments were readily applicable to routine exposure monitoring due to non-specificity, lack of portability, difficulty of use, and high cost. The field team thus refined an in-depth nanoparticle research effort into a portable procedure that has been successfully used in a variety of facilities that handle or create engineered nanoparticles. The NEAT utilizes portable direct-reading instrumentation (condensation and optical particle counters) supplemented by filter-based air samples (source-specific and personal breathing zone [PBZ]). The use of the filter samples are crucial for identification purposes because particle counters are generally insensitive to particle source or composition and make it difficult to differentiate between incidental and process-related nanoparticles using number concentration alone. Results from using this technique at 12 facilities demonstrated that this technique is a viable means to identify potential engineered nanoparticle emissions.

Due to space limitations, this paper will present only a brief example of the findings. The purpose of this paper is to describe the technique which can be used by other health and safety professionals in the nanotechnology field.

2 METHOD

2.1 Instrumentation and Materials

The following instrumentation is used by NIOSH; however, use does not constitute endorsement. Equivalent instrumentation could be substituted.

TSI model 3007 (or model 8525) (TSI Inc, Shoreview, MN), handheld condensation particle counter (CPC). The CPC provides a non-specific measure of the total number of particles independent of chemical identity per cubic centimeter of air (P/cc). The measurable range is between 10 nanometers (nm) and 1,000 nm (1 µm), or between 20 nm and 1,000 nm for model 8525.

ART Instruments Hand Held Particle Counter (HHPC-6, ART Instruments, Grants Pass, Oregon). The HHPC-6, optical particle counter (OPC) can measure the total number of particles per liter of air (P/L) independent of chemical identity within six specific size ranges. The OPC used by the field team consists of the following size ranges:

300 nm; 500 nm; 1,000 nm; 3,000 nm; 5,000 nm, and 10,000 nm.

Appropriate filter-based air sampling media were selected based on the engineered nanoparticle type and desired analytical information (e.g. mixed cellulose ester [MCE] filters for metals or metal oxides, quartz fiber filters [QFF] for elemental carbon) and MCE or polycarbonate membrane filters for determination of particle morphology using transmission electron microscopy (TEM) or scanning electron microscopy (SEM), each with energy dispersive X-ray spectrometry (EDS) capabilities.

Air sampling pumps capable of sampling at relatively high flow rates (e.g. 7 liters per minute), to collect the filter samples.

2.1 Sampling Strategy

The initial assessment involves identifying the potential source(s) of engineered nanoparticle emissions by reviewing the type of process, process flow, material inputs and discharges, and work practices. Once potential sources of emissions were identified, the field team member (industrial hygienist):

- Conducted an observational walkthrough survey of the production area and processes to identify potential sources of emissions
- Determined the frequency and duration of each operation and the type of equipment used for handling and containment of the material
- Determined the presence/absence of general and local exhaust ventilation (LEV). This initial assessment included identifying points of potential system failure that could result in emission from the containment/control system (e.g., hole in duct, deteriorated sealing gasket)
- Determined the process points where containment is breached (e.g., opening system for product retrieval or for cleaning)

2.2 Particle Number Concentration Sampling

Background sampling

Addressing the influence of background particle number concentration on engineered nanoparticles is an important aspect of measuring particle number concentration. Ideally, a measurement of the background particle number concentration is taken with the CPC and OPC *before* the processing or handling of engineered nanoparticles begins. Measurements of background particle number concentrations are repeated after the processing and manufacturing has ended. An average background concentration is then computed and subtracted from the measurements made during processing, manufacturing or handling of engineered nanoparticles. This approach is acceptable only if the background particle number concentration remains relatively stable throughout the measurement period and particle emissions from the process are sufficiently elevated above background.

If the background particle number concentration is high (value depends on the industry), or varies considerably between areas that are considered to be at background, then there may be a source of incidental nanoparticles in the area. Incidental nanoparticles may be generated from a variety of sources, including vacuum pumps, natural gas heating units, gasoline/propane/diesel powered fork lift trucks, or other activities such as welding, soldering, or heat-sealing. The CPC and OPC can be used to locate processes or activities that may be the source of incidental nanoparticles. Outdoor or recirculated air supply from the building ventilation system should also be considered as a possible source of nanoparticles [2]. For other situations, the issue of adjusting measurement data based on background particle number concentration becomes much more complex and is generally outside the scope of the assessment technique described here.

Suspected Emission Sources

Once the initial background measurements have been obtained, the industrial hygienist used the CPC and OPC to determine the particle number concentration at different locations near the emission source (e.g., process/task, potential leak points in the ventilation system). Multiple particle number concentration data were collected before, during, and after each task or operation to identify specific factors (e.g., controls, worker interaction, work practices) that may affect particle number concentration measurements. This information was used to identify processes, locations and personnel for filter-based air sampling.

2.3 Filter-based Area Air Sampling

A pair of filter-based, air samples were collected at process/task locations and/or workers engaged in process operations where suspected engineered nanoparticle emissions may occur, as identified by the CPC and OPC results.

Filter-based air samples provide more specific information on the engineered nanoparticle of interest (e.g., chemical composition, mass, size, shape, degree of agglomeration). The pair of air samples includes one sample analyzed for elemental mass concentration and the other analyzed for particle characterization by electron microscopy. For example, samples might be collected for metals determination (e.g., using NIOSH Method 7300 or 7303) or elemental carbon (e.g. using NIOSH Method 5040) depending on the chemical composition of the engineered nanoparticle, in addition to collection of a sample for particle characterization (e.g., size, shape, dimension, degree of agglomeration) by TEM using the measurement techniques specified in NIOSH Method 7402 or by SEM using measurement techniques specified in NIOSH Method 7404 [3].

The source-specific air samples were collected as close as possible (e.g. at the opening of a reactor during product harvesting) to the suspected emission source to determine the "worst-case scenario" and increase the probability of capturing the engineered nanoparticles. Sampling duration matched that of the task or specific process. Because the duration of the tasks associated with the potential airborne release of engineered nanoparticles was short (e.g., minutes), a relatively high air sampling flow rate was used (approximately 7 liters per minute) to ensure adequate loading on the filter media. In general, filter samples were collected for the duration of a specific task, normally 15–30 minutes.

A pair of background filter samples were collected far enough from production (e.g., in an adjoining room) to serve as an indicator of ambient background particle identification and concentration.

Figure 1: The nanoparticle emission assessment technique consists of an optical particle counter, 2 filter samples and a condensation particle counter.

2.4 Personal Air Samples

When possible, filter-based PBZ air samples were collected on workers likely to be exposed to engineered nanoparticles (e.g., engaged in handling/operating equipment previously identified by the CPC/OPC as emitting engineered nanoparticles). PBZ samples were analyzed in the same manner as the source-specific air samples (e.g., by TEM and mass).

3 RESULTS

3.1 Facilities, processes and controls evaluated

Facilities evaluated included research and development laboratories, pilot plants, and manufacturing locations engaged in the production or handling of single-walled and multi-walled carbon nanotubes (CNT), carbon nanofibers, fullerenes, carbon nanopearls, metal oxides, quantum dots, Nylon 6 nanofiber and a silica-iron compound. Tasks evaluated included transfer operations, weighing, drying, spraying, chopping, sonication, cleaning. Processes used to produce the engineered nanoparticles included pulsed vapor deposition, chemical vapor deposition, radiofrequency induction plasma and a spray deposition chamber. Engineering controls used at the facilities included laboratory fume hoods, local exhaust ventilation, 3-sided exhausted enclosures, negative pressure rooms and complete enclosures.

3.2 Summary of background particle number concentrations

Background particle number concentrations varied widely between facilities and ranged from 700 – 33,500 P/cc based on the CPC, and between 250 – 121,300 P/L based on the OPC.

Type of facility	**CPC results, P/cc 10 – 1,000 nm**	**OPC results, P/L 300 – 500 nm**
Carbonaceous Materials (n=5 facilities)	720 –19,500	250 – 13,700
Metals and metal oxides (n=5 facilities)	2,340 – 33,500	7,580 – 89,000*
Quantum dots and Nylon 6 (n=2 facilities)	1,670 – 15,410	60 – 121,300*

* Results exceed the upper dynamic limit of the OPC, 70,000 P/L

Table 1: Example background particle number concentrations at various nanoparticle facilities

3.3 Example particle number concentrations from various nanoparticle facilities and processes

Background-adjusted, process specific, particle number concentrations ranged from zero to 144,800 P/cc (CPC), and from zero to >300,000 P/L on the smallest size range (300-500 nm) on the OPC. Several measurements exceeded the upper dynamic limit of 100,000 P/cc for the CPC and 70,000 P/L for the OPC. Example particle number concentrations measured at several of the processes are presented in Table 2. Metal oxides were monitored at one site before and after the use of a HEPA-filtered LEV and demonstrated that the LEV was highly effective in controlling the release of the nanoparticles [4]. Also presented in Table 2 are data from incidental nanoparticle sources (e.g., gas powered forklift and arc welder).

Process	CPC results P/cc 10–1,000 nm	OPC results P/L 300 – 500 nm
Opening CNT reactor with no engineering controls	42,400	348
Weighing fullerenes, no engineering controls	1,476	53,119
Metal oxide spray drier drum change out, no engineering controls	144,800*	217,271*
Unloading metal oxide calciner trays, no controls	15,522	109,441*
Weighing metal oxides, no controls	814	5,403
Opening metal oxide reactor, no controls	16,917	47,350
Opening metal oxide reactor, local exhaust ventilation used	998	3,058
Propane forklift (incidental particles)	45,021	N/A
Electric arc welding (incidental particles)	84,590	262,070*

* Results exceed the upper dynamic limit of the instrumentation of 100,000 p/cc for the CPC and 70,000 P/L for the OPC. N/A = not applicable

Table 2: Example particle number concentrations collected at various nanoparticle facilities.

3.4 Elemental and microscopy results

Elemental mass and electron microscopy analysis of filter samples collected at the 12 facilities were successfully used to verify that the particles measured with the particle counters were of the same composition of the nanoparticles of interest. In facilities where incidental nanoparticles were measured, the analysis of the filters demonstrated that the particles measured by the CPC and OPC were not engineered nanoparticles produced or handled at the facility. This finding confirmed that the particles measured by the CPC and OPC were incidental to the nanoparticle process.

4 DISCUSSION

The NEAT has been used and refined by NIOSH over the past 3 years and brief examples of the results were included in this report. This technique may be easily adopted by health and safety professionals in the nanotechnology field.

Note that source specific samples collected close to a suspected point of emission are intended to increase the probability of capturing engineered nanoparticles and allow for identification of “worst-case scenarios.” **Therefore, results from this type of sampling should not be interpreted as representative of worker exposure**. However, samples collected in such a fashion can serve as an indicator of emissions and the possible need for controls.

While this issue is not unique to particle number concentration measurements, orders of magnitude difference can exist in particle number concentrations, depending on the day, time, number and types of sources of particle emissions. Monitoring over several days, months or seasons will provide a better estimation of potential emissions and subsequent worker exposure and should be considered by industrial hygienists responsible for occupational safety and health at an engineered nanoparticle facility (as opposed to NIOSH industrial hygienists who are often on-site for a limited amount of time).

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