Organisation de Coopération et de Développement Économiques
Organisation for Economic Co-operation and Development

18-Jun-2009

English - Or. English

ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY

SERIES ON THE SAFETY OF MANUFACTURED NANOMATERIALS
Number 11

EMMISION ASSESSMENT FOR IDENTIFICATION OF SOURCES AND RELEASE OF AIRBORNE MANUFACTURED NANOMATERIALS IN THE WORKPLACE: COMPILATION OF EXISTING GUIDANCE

JT03266895

ENV/JM/MONO(2009)16
Unclassified

English - Or. English

OECD Environment, Health and Safety Publications
Series on the Safety of Manufactured Nanomaterials

No.11

EMISSION ASSESSMENT FOR THE IDENTIFICATION OF SOURCES AND RELEASE OF AIRBORNE MANUFACTURED NANOMATERIALS IN THE WORKPLACE: COMPILATION OF EXISTING GUIDANCE

IOMC
INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD

Environment Directorate
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT
Paris 2009

Also published in the Series of Safety of Manufactured Nanomaterials:

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No. 2, *Current Developments/ Activities on the Safety of Manufactured Nanomaterials: Tour de table at the 1st Meeting of the Working Party on Manufactured Nanomaterials (2006)*

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No.11, *Emission Assessment for the Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance*

ABOUT THE OECD

The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Asia and Pacific region, as well as the European Commission, meet to co-ordinate and harmonise policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised committees and working groups composed of member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's workshops and other meetings. Committees and working groups are served by the OECD Secretariat, located in Paris, France, which is organised into directorates and divisions.

The Environment, Health and Safety Division publishes free-of-charge documents in ten different series: **Testing and Assessment**; **Good Laboratory Practice and Compliance Monitoring**; **Pesticides and Biocides**; **Risk Management**; **Harmonisation of Regulatory Oversight in Biotechnology**; **Safety of Novel Foods and Feeds; Chemical Accidents; Pollutant Release and Transfer Registers; Emission Scenario Documents; and the Safety of Manufactured Nanomaterials.** More information about the Environment, Health and Safety Programme and EHS publications is available on the OECD's World Wide Web site (http://www.oecd.org/ehs).

This publication was developed in the IOMC context. The contents do not necessarily reflect the views or stated policies of individual IOMC Participating Organizations.

The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The participating organisations are FAO, ILO, OECD, UNEP, UNIDO, UNITAR and WHO. The World Bank and UNDP are observers. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

FOREWORD

The OECD Joint Meeting of the Chemicals Committee and Working Party on Chemicals, Pesticides and Biotechnology (the Joint Meeting) held a Special Session on the Potential Implications of Manufactured Nanomaterials for Human Health and Environmental Safety (June 2005). This was the first opportunity for OECD member countries, together with observers and invited experts, to begin to identify human health and environmental safety related aspects of manufactured nanomaterials. The scope of this session was intended to address the chemicals sector.

As a follow-up, the Joint Meeting decided to hold a Workshop on the Safety of Manufactured Nanomaterials in December 2005, in Washington, D.C. The main objective was to determine the "state of the art" for the safety assessment of manufactured nanomaterials with a particular focus on identifying future needs for risk assessment within a regulatory context.

Based on the conclusions and recommendations of the Workshop [ENV/JM/MONO(2006)19] it was recognised as essential to ensure the efficient assessment of manufactured nanomaterials so as to avoid adverse effects from the use of these materials in the short, medium and longer term. With this in mind, the OECD Council established the OECD Working Party on Manufactured Nanomaterials (WPMN) as a subsidiary body of the OECD Chemicals Committee. This programme concentrates on human health and environmental safety implications of manufactured nanomaterials (limited mainly to the chemicals sector), and aims to ensure that the approach to hazard, exposure and risk assessment is of a high, science-based, and internationally harmonised standard. This programme promotes international co-operation on the human health and environmental safety of manufactured nanomaterials, and involves the safety testing and risk assessment of manufactured nanomaterials.

This document is intended to provide information on activities of the WPMN related to the safety of manufactured nanomaterials. The Working Party endorsed this report at its 5th Meeting on March 2009. This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology of the OECD.

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THE WORKING PARTY ON MANUFACTURED NANOMATERIALS (WPMN)

The Working Party on Manufactured Nanomaterials[1] was established in 2006 to help member countries efficiently and effectively address the safety challenges of nanomaterials. OECD has a wealth of experience in developing methods for the safety testing and assessment of chemical products.

The Working Party brings together more than 100 experts from governments and other stakeholders from: a) OECD Countries; b) non-member economies such as Brazil, China, the Russian Federation, Singapore and Thailand; and **c**) observers and invited experts from UNEP, WHO, ISO, BIAC[2], TUAC[3], and environmental NGOs.

Although OECD member countries appreciate the many potential benefits from the use of nanomaterials, they wished to engage, at an early stage, in addressing the possible safety implications at the same time as research on new applications is being undertaken.

The Working Party is implementing its work through eight main areas of work to further develop appropriate methods and strategies to help ensure human health and environmental safety:

Development of a Database on Human Health and Environmental Safety (EHS) Research;
EHS Research Strategies on Manufactured Nanomaterials;
Safety Testing of a Representative Set of Manufactured Nanomaterials;
Manufactured Nanomaterials and Test Guidelines;
Co-operation on Voluntary Schemes and Regulatory Programmes;
Co-operation on Risk Assessment;
The role of Alternative Methods in Nanotoxicology; and
Co-operation on Exposure Measurement and Exposure Mitigation.

Each area of work is being managed by a steering group, which comprises members of the WPMN, with support from the Secretariat. Each steering group implements its respective "operational plans", each with their specific objectives and timelines. The results of each project are then evaluated and endorsed by the entire WPMN.

This document was prepared by the WPMN steering group 8 leading the work on *Co-operation on Exposure Measurement and Exposure Mitigation*. The Working Party endorsed this report at its 5th Meeting on March 2009.

[1] Updated information on the OECD's Programme on the Safety of Manufactured Nanomaterials is available at: www.oecd.org/env/nanosafety
[2] The Business and Industry Advisory Committee to the OECD
[3] Trade Union Advisory Committee to OECD.

CO-OPERATION ON EXPOSURE MEASUREMENT AND EXPOSURE MITIGATION

In November 2007 the OECD Working Party on Manufactured Nanomaterials decided to start work on **Co-operation on Exposure Measurement and Exposure Mitigation**. A steering group lead by the US, and comprising delegates from the WPMN was tasked with developing this work.

The operational plan outlines three phases of work: 1) exposure in occupational settings; 2) exposure to humans resulting from contact with consumer products and environmental releases of manufactured nanomaterials; and 3) exposure to environmental species resulting from environmental releases of manufactured nanomaterials including releases from consumer products containing manufactured nanomaterials.

The objectives of phase 1 are described as:

- To identify and compile guidance information for exposure measurement and exposure mitigation for manufactured nanomaterials in occupational settings, including manufacture and use of products in industrial, institutional and commercial settings; and
- To analyze existing guidance information for their adequacy in addressing manufactured nanomaterials, identify issues that are unique to manufactured nanomaterials, and prepare recommendations for next steps to be undertaken by the WPMN.

As part of Phase 1, the WPMN decided to develop project on *Emission Assessment for Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace – Compilation of Existing Guidance*. This document aims at providing guidance for health and safety professionals, specifically for industrial/occupational hygienists[4]. It should be seen as one element within the frame of complete exposure assessment consisting of nanomaterial emission sampling and measurement of nanomaterials and their subsequent possible toxicological effects.

More information about the work of the WPMN, as well as publications and updates on efforts o governments and other stakeholders to address safety issues of nanomaterials is available at http://www.oecd.org/env/nanosafety.

[4] "industrial hygienist" and "occupational hygienist" are used in this document interchangeably.

EMISSION ASSESSMENT FOR IDENTIFICATION OF SOURCES AND RELEASE OF AIRBORNE MANUFACTURED NANOMATERIALS IN THE WORKPLACE – COMPILATION OF EXISTING GUIDANCE

1. Introduction

Exposure assessment is a critical component of risk assessment and risk management programs. A number of countries have initiated surveys of exposures in nanotechnology workplaces and developed their own exposure assessment protocols. In Germany, BAuA, BGIA, IUTA Industry and ICBA have conducted such surveys (Kuhlbusch et al, 2006, 2008, 2009). In USA, the National Institute for Occupational Safety and Health (NIOSH) formed a field team, which has been assessing workplace processes, materials, and control technologies associated with nanotechnology since 2006[5]. As a result of such activities, evaluation of instrumentation for characterizing nanomaterials in workplace environments[6], as well as emission assessment guidance to semi-quantitatively evaluate workplaces where release of manufactured nanomaterials may occur (see e.g. NIOSH, 2008) became available.

At European level a number of different activities are currently pursued including identification of sources of manufactured nanomaterials, characterization of particles, sampling and on-line detection including the assessment of various methodologies, personal exposure, qualitative assessment of dermal exposure, work on the aerosol dynamics of nanomaterials (adherence, coagulation, aggregation and/or agglomeration), techniques addressing the background assessment versus the specific emission of manufactured nanomaterials up to new process developments. More information and an information update of these activities can be found in the respective presentations of various EU research projects (e.g. NANOSAFE[7], NANOSH[8], NANOSAFE2, NANOTRANSPORT[9], NANODEVICE[10], IMPART, etc.)[11]. Moreover, the recently completed NANOSAFE2008 conference in Grenoble, 3-5 November 2008 (NANOSAFE, 2008) and OECD's WPMN Workshop on Workshop on Exposure Assessment and Exposure Mitigation in Frankfurt on 20 October 2008 (OECD, 2009) showed the possibilities of options available for exposure measurements and also highlighted that it is now time to start with the formal

[5] www.cdc.gov/niosh/docs/2008-121/; www.cdc.gov/niosh/docs/2008-120 ; Methner et al, 2007; Methner, 2008.

[6] See for example, Table G-2 in NIOSH, 2007.

[7] See NANOSAFE and NANOSAFE2 at: http://www.nanosafe.org/

[8] http://www.ttl.fi/Internet/partner/Nanosh/

[9] http://research.dnv.com/nanotransport/

[10] See presentation at the EC Workshop held 17+18 April 2008 on ftp://ftp.cordis.europa.eu/pub/nanotechnology/docs/final-version.pdf

[11] On the following web-sites: ftp://ftp.cordis.europa.eu/pub/nanotechnology/docs/final_report.pdf and http://www.temas.ch/Impart/ImpartProj.nsf/vwUICatalogAll/CB605CB477B304D0C125746B004FC48D?OpenDocument&lang=en

validation of the promising exposure measurements, sampling and design approaches. Furthermore, the European Agency for Safety and Health at Work established a Risk Observatory that includes also nanomaterials and addresses exposure to these materials during manufacturing and use that may occur through inhalation, dermal contact and ingestion[12].

To ensure consistency of collected data and to facilitate exchange of data by providing guidance on measurement techniques and sampling protocols for assessments of inhalational and dermal exposures in the workplace, OECD's Working Party on Manufactured Nanomaterials (WPMN) agreed to start work on *recommendations on measurement techniques and sampling protocols for inhalational and dermal exposures in the workplace*. This project was implemented by the WPMN Steering Group 8 (SG8) leading the work on *Co-operation on Exposure Measurement and Exposure Mitigation*.

This document is the outcome of the OECD WPMN project which was mentioned above. This project was originated at the US National Institute for Occupational Safety and Health (NIOSH) field team and it incorporated inputs from OECD steering group that lead this work. It is intended to provide guidance for health and safety professionals, specifically for industrial/occupational hygienists[13].

This document should be seen as a component of the overall work of the programme on the safety of manufactured nanomaterials, which is been developed by OECD's WPMN. It is one element within the frame of complete exposure assessment consisting of nanomaterial emission sampling and measurement from different sources within the production process including different routes; and the fate of nanomaterials in different compartments such as air, water and soil including possible aspects linked to their aggregation and agglomeration, absorption of nanomaterials by the body and their subsequent possible toxicological effects. Separate future documents should build on this emission guidance document to cover exposure assessment through relevant routes such as inhalation and skin contact. Exposure assessment combined with hazard assessment conducted through WPMN Sponsorship Program for Safety Testing of Representative Nanomaterials[14] will inform guidance on exposure mitigation activities including engineering techniques and personal protective equipment.

2. Scope

Since there are currently no exposure limits for the majority of manufactured nanomaterials, a qualitative assessment is used to determine whether any airborne releases of manufactured nanomaterials occur. This assessment, which compares particle concentrations at the emission source to background particle concentrations, provides a qualitative means for determining whether existing measures are adequate for controlling nanomaterial emissions or if additional controls might be needed. Results from this assessment should not be interpreted as representative of worker exposure.

The nanomaterial emission assessment guidance describes the initial assessment and optional sampling. The initial assessment uses complimentary approaches to semi-quantitatively determine particle number concentration, shape, and mass concentration, together with a qualitative indication of particle size. It begins with an observational walkthrough survey of the facility by the industrial/occupational hygienist to gain a better understanding of each process and determine potential emission source(s) of manufactured nanomaterials as outline in Figure 1. At potential emission sources, direct-reading, handheld instruments (CPC and OPC) are used to determine particle number concentrations. If elevated concentrations of suspected nanoparticles are detected at potential emission sources, relative to the background particle

[12] see http://osha.europa.eu/en/sub/riskobservatory/teaser/nanotechnologies

[13] Please note that "industrial hygienist" and "occupational hygienist" are used in this document interchangeably.

[14] See www.oecd.org/env/nanosafety

number concentrations, then a pair of filter-based, source-specific air samples are collected (e.g. using 37-mm diameter filter cassettes) with one sample analyzed by electron microscopy (EM) such as Transmission EM (TEM) or Scanning EM (SEM) for particle identification and characterization, and the other used for determining the elemental mass concentration. A second pair of filter-based air samples may also be collected in the personal breathing zone of workers. Breathing zone samples are analyzed in the same manner as the area air samples (i.e., by TEM and elemental mass). Personal cascade impactors may be used to separate the large particle fraction.

Surface sampling may be added to the initial assessment if the potential exists that nanomaterials are contaminating surfaces by settling from air, by being released due to material spills, or via migration of material from one part of the facility to another (see 4.3.3.2).

This guidance on nanomaterial emission assessment provides a simple semi-quantitative determination of nanomaterial release and may be useful to health and safety professionals, specifically for occupational hygienists, who are interested in determining whether release of nanomaterials occurs in the workplace. It could be also useful in semi-quantitative estimate of personal exposures (see e.g. Koshi, 1980), which could guide selection of appropriate exposure mitigation techniques (for dermal protection see e.g. Wendel-de-Joode et al, 2003).

3. Air Sampling Instrumentation and Filter Media

The following minimum set of instrumentation is recommended to conduct the initial assessment:

- Handheld Condensation Particle Counter (CPC).

  CPC (ISO/PWI 2789: 2008) provides a measure of the total number of particles independent of chemical form per cubic centimetre of air (P/cc). Minimum requirements for this assessment are: particle size range between 10 nanometers (nm) and 1,000 nm (1 μm); the range of detection from 0 to 100,000 P/cc.
- Handheld Optical Particle Counter (OPC).

  OPC (ISO 21501-4: 2007, ISO/DIS 21501-1: 2008) can measure the total number of particles (particles per liter of air) within a number of specific size ranges depending on the model. A minimum number required for this assessment is four as follows: 300 - 500 nm; 500 - 1,000 nm; 1,000 - 10,000 nm, and > 10,000 nm.
- Appropriate air sampling filter media (e.g. mixed cellulose ester, quartz fiber filter) are selected depending on nanomaterial type and desired analytical information (e.g., determination of particle morphology using TEM or SEM, elemental analysis for metals, elemental analysis for carbon). Please note, that a specially prepared filter with a TEM grid can be used, so preparation of the filter prior to TEM analysis is not necessary any longer (Tsai et al, 2008).
- Air sampling pumps capable of sampling at high flow rates (up to 10 liters per minute or other flow rate depending upon the duration of the task, desired characterization method and the appropriate standard, if a standard is available).
- TP (Thermal Precipitator) collects nanoscale particles on a Si-Wafer, while ElectroStatic Precipitator (ESP) collects nanoscale particles on carbon TEM grids. Following SEM-analysis these samplers provide information about the particle morphology and chemical structure.
- Sampling pump flow calibrator
- Optional surface sampling supplies such as substrate, disposable 10 cm x 10 cm templates, sterile containers and nitrile gloves for handling media (see 4.3.3.2).
- If desired, personal cascade impactor or respirable cyclone sampler (see 4.3.3.1).

- If desired, cassette conductive cowl (see 4.3.3.1).

4. Evaluation of Potential Releases of Manufactured Nanomaterials

4.1 Identify Potential Sources of Emissions

The overall purpose of this step is to develop a list of target areas and tasks that will be evaluated with the particle analyzers.

The initial assessment involves identifying the potential sources of manufactured nanomaterial emissions by reviewing the type of process, process flow, material inputs and discharges, tasks and work practices. When available, literature (e.g. MSDS, records of feedstock materials) is reviewed to gain an understanding of the engineered nanomaterials being produced or used, including their physicochemical properties such as size, shape, solubility, and reactivity. Once the potential sources of emissions have been identified from the process review, the industrial hygienist (or other qualified person):

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

4.2 Conduct Particle Number Concentration Sampling

4.2.1 Background measurements

Determining the contribution of background particle concentrations on measurements made for the particles of interest (e.g., manufactured nanomaterials) is an important evaluation for assessing the possible airborne release of manufactured nanomaterials.

Ideally, during the initial assessment, an industrial/occupational hygienist (or other qualified person) will determine the average airborne particle number concentrations at various processes and adjacent work areas with the CPC and OPC *before* the processing or handling of nanomaterials begins (Table 1). If the background particle number concentrations are high (values are relative and will vary with processes and facilities), an assessment is made as to whether there may be a source of incidental nanoscale particles in the area. Incidental nanoscale particles may be generated from a variety of sources, including vacuum pumps, natural gas heating units, gasoline/propane/diesel powered fork lift trucks, or other combustion or heat generating activities such as welding, soldering, or heat-sealing. The CPC and OPC can be used to check these sources for incidental nanoscale particle releases. Outdoor or re-circulated air supply from the building ventilation system should also be considered as a possible source of nanoscale particles (Peters et al. 2006).

Measurements of background particle concentrations will be repeated after the active processing, manufacturing or handling of the nanomaterial has ended. An average background concentration is then computed and subtracted from measurements made during processing, manufacturing or the handling of manufactured nanomaterials. This approach is acceptable only if background particle counts remain relatively stable throughout the measurement period and particle emissions from the process under investigation are sufficiently elevated above background. For other situations, correcting for particle background concentrations becomes more complex requiring additional sampling over an extended time

period to determine the source(s) and magnitude of background particle concentrations. This type of evaluation is generally outside the scope of the initial assessment described here.

4.2.2 Area sampling

Once initial background particle concentrations have been determined, measurements of airborne particle concentrations and size ranges are made with the CPC and OPC simultaneously at locations near the suspected or likely emission source (e.g., opening a reactor, handling product, potential leak points in the ventilation system). Airborne particle concentrations are determined before, during, and after each task or operation to identify those factors (e.g., controls, worker interaction, work practices) that may affect airborne particle concentrations. This information is used to identify processes, locations, and personnel for filter-based air sampling (4.3).

4.3 Conduct Filter-based Area and Personal Air Sampling

4.3.1 Area air sampling

A pair of filter-based, air samples are collected at process/task locations and/or workers engaged in process operations where suspected manufactured nanomaterial emissions may occur, based on air sampling results using the CPC and OPC.

Filter-based area air samples provide more specific information on the manufactured nanomaterial of interest (e.g., size, shape, mass). The pair of air samples includes one sample analyzed for elemental mass and one sample analyzed by electron microscopy. For example, one sample might be collected for metal determination (e.g., NIOSH Method 7303) or elemental carbon (e.g., NIOSH Method 5040) depending on the composition of the manufactured nanomaterial. The other sample would be collected for particle characterization (e.g., size, shape, dimension, degree of agglomeration) by TEM or SEM using the measurement techniques specified in NIOSH Methods 7402, 7404, or other equivalent methods (NIOSH, 1994).

The source-specific air samples are collected as close as possible to the suspected emission source but outside of any existing containment, to increase the probability of detecting any possible release of engineered nanomaterials. Sampling duration generally matches the length of time in which the potential exposure to the engineered nanomaterial exists at the task or specific process. In cases where the duration of the tasks associated with the potential airborne release of nanomaterials is short (e.g., minutes), a relatively high air sampling flow rate may be required (up to 10 liters per minute depending on the characterization method, see also Table 2) to ensure adequate particle loading on the filter media. If specific information is desired on the worker's potential exposure to the engineered nanomaterial then PBZ samples should be collected using the two- sample filter-based sampling strategy described above.

If the particle number concentrations (using CPC or OPC) are substantially high, then shorter sampling times for the TEM or SEM sample may be necessary to avoid overloading the filter and interfering with particle characterization. The specific sampling time should be based on direct-reading instrument results and professional judgment of the industrial hygienist. In general, filter samples are collected for the duration of a given task, normally 15–30 minutes. If the direct-reading instruments indicate a high particle number concentration the sampling time can be shortened to 5–10 minutes, or both a short- and long-duration sample may be collected to ensure an adequate sample for electron microscopy analysis. See Table 2 for additional sampling time guidance. However, the sampling times in Table 2 were based on collection of asbestos fibers by NIOSH Method 7402 and may not be applicable for much smaller manufactured nanoscale particles.

A minimum of two background filter samples are collected distant from the potential sources of manufactured nanomaterial exposure to serve as an indicator of ambient particle identification and concentration.

4.3.2 Personal air sampling

When possible, personal breathing zone (PBZ) air samples are collected on workers likely to be exposed to manufactured nanomaterials (e.g., engaged in active handling of nanomaterials or operating equipment previously identified as emitting nanomaterials). If measurements obtained with the CPC and OPC indicate that nanoscale particles are being emitted at a specific process where a worker is located, then the collection of PBZ samples may be warranted.

PBZ samples are analyzed in the same manner as the area air samples (e.g. by TEM and for elemental mass). It may be necessary to collect samples at a relatively high flow rate (e.g., up to 10 liters per minute) if the duration of the task and the resulting potential exposure is short. Recently personal sampling for TEM analysis was improved by using a TEM grid fitted on a coated filter (Tsai et al., 2008).

4.3.3 Optional sampling

4.3.3.1 Air sampling

In the event that measurements made by the OPC indicate a large fraction (over 50%) of particles exceeding 1000 nm in size, the use of a personal cascade impactor or respirable cyclone sampler in tandem with a filter-based air sampling cassette may be required for both the elemental mass and TEM/SEM analysis to eliminate large particles, that may interfere with analysis and be of limited interest. The use of an impactor or cyclone will require using a flow rate appropriate for the particle cut size and is usually in the range of 1.7–2.5 liters per minute. Open-face, and impactor or cyclone samples may be collected side by side to allow a more thorough interpretation of analytical results. Additionally, if it is anticipated that the particles of interest will have a tendency to be electrostatically attracted to the sides of the plastic air sampling cassette, a conductive cowl may be necessary to eliminate particle loss and subsequent underestimation of the airborne particle concentration. The use of a personal cascade impactor, respirable cyclone, or conductive cowl is made at the discretion of the industrial hygienist (or other qualified person).

If the facility is manufacturing or using TiO_2, then the sampling could include the sampling recommendations found in the NIOSH *Draft Document: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide*[15], which recommends collecting a mass-based airborne measurement using NIOSH Method 0600.

4.3.3.2 Surface sampling

Surface sampling to detect the presence of manufactured nanomaterials is not routinely a part of the initial assessment but may be conducted to determine if surface contamination exists. Surface sampling does not provide size specific information but may be useful for determining whether manufactured nanomaterials are contaminating non-production work areas. It could be also used as a tool for determining the effectiveness of existing control measures in reducing manufactured nanomaterial exposure levels. The decision to collect surface samples is made in the field at the discretion of the industrial/occupational hygienist (or other qualified person), and is dependent on direct observation and the nanomaterial of interest. For example, surface sampling was completed at a quantum dot facility after observing dusty surfaces in areas adjacent to the production area. In order to determine if the dust was contaminated with

[15] See www.cdc.gov/niosh/review/public/TIo2/default.html

quantum dots, surface samples were collected and analyzed for the chemical components of the quantum dots produced by that facility. Surface wipe samples can be collected using pre-moistened substrate in accordance with a standard method such as NIOSH Method 9102 for elements (NIOSH, 1994). When collecting wipe samples, the following steps should be followed:

- Don a pair of nitrile disposable gloves;
- Wipe the surface within a disposable 10 cm x 10 cm template using four horizontal s-shaped strokes;
- Fold the exposed side of the wipe in and wiping the same area with four vertical s-shaped strokes;
- Fold the wipe, exposed side in, and placing it into a sterile container.

Gloves and template are discarded after each sample collection to eliminate the possibility of cross-contaminating successive samples. Wipe samples may be collected from undisturbed horizontal surfaces throughout the facility at locations suspected to be contaminated and in areas expected to be free of manufactured nanomaterials. Wipe samples are analyzed following an appropriate standard method for the chemical substance of interest.

4.4 Quality Assurance and Quality Control

To ensure valid exposure measurements, the following quality assurance and control steps should be taken:

- Use factory calibrated direct-reading particle analyzers;
- Perform daily zero checks on all particle counters before each use;
- Calibrate pumps before and after each sampling day;
- Submit for analysis any process, background, and bulk material samples along with field and media blanks to an accredited laboratory for analysis (in USA, accredited by American Industrial Hygiene Association).

A "Reference Material" (RM) is a material having a proven and sufficient homogeneity and stability in terms of a defined intended use. RMs can be used for different purposes, including for quality control, calibration of measurement approaches, and assessment of laboratory proficiency or test method performance. Currently, there exist a small number of reference materials in the field of manufactured nanomaterials [e.g. gold nanoparticles (RM 8011, RM 8012, RM 8013) from the U.S. National Institute of Standards and Technology and colloidal silica (RM-N° IRMM-304) from the European Commission, Joint Research Centre – Institute for Reference Materials and Measurements (IRMM), Geel, Belgium[16]. They are spherical model materials and are certified primarily for size and can, hence, be applied for calibration and quality control of instruments measuring particle size. The current absence of agreed exposure metrics, e.g. size distribution, number concentration and/or surface area, and standardised test protocols is identified as a major obstacle for RM production, because agreed and harmonised methods are required.

4.5 Data Interpretation

4.5.1 Particle Size

Since the size of airborne manufactured nanomaterials and the degree of agglomeration may be unknown at the time of sample collection, the use of direct-reading, particle sizing/counting instruments may provide a semi-quantitative indication of the magnitude of potential emissions, provided background

[16] For additional information: http://ec.europa.eu/dgs/jrc/index.cfm?id=2820&obj_id=220&dt_code=HLN&lang=en

particle number substraction can be successfully accomplished. The particle number concentration measurements taken with CPC and OPC will provide a measurement of particles larger than the ISO definition of nanoparticles (approximately 1 to 100 nm) [ISO TS 27687:2008]. However, the two particle counters can be used simultaneously to obtain a semi-quantitative size differential evaluation of the aerosol being sampled. The CPC provides a measure of total particles per cubic centimeter of air in the size range of 10-1,000 nm. The OPC can provide the total number of particles per liter of air within a minimum of four specific size ranges: 300 - 500 nm; 500 - 1,000 nm; 1,000 - 10,000 nm, and > 10,000 nm. If necessary, the data from the CPC and OPC can be used together to determine the number concentration of nanoscale particles. For example, a high particle number concentration on the CPC, in combination with a high particle number concentration in the small size range (300-500 nm) on the OPC, may indicate the possible presence of nanoscale particles. Conversely, a low CPC particle number concentration, in combination with a high OPC particle number concentration in the larger size range (> 1,000 nm) may indicate the presence of larger particles and/or nanoscale particle agglomerates. These assumptions of nanoscale particles versus larger particles and/or nanoscale particle agglomerates may be verified by TEM or SEM analysis.

4.5.2 Selectivity

Selectivity is a critical issue when characterizing exposure using particle number concentration. Airborne nanoscale particles are present in many workplaces and often originate from multiple sources such as combustion, vehicle emissions, and infiltration of outside air. Particle counters are generally not selective to particle source or composition, making it difficult to differentiate between incidental and process-related particles using number concentration alone. The CPC and OPC are used to identify sources of nanoscale particles and the filter-based samples are used to verify the size, shape, and chemical composition of the nanoscale particles with the goal of differentiating between incidental nanoscale particles and manufactured nanomaterials.

4.5.3 Limitations

The emission assessment technique does have some limitations including:

- Although this issue is not unique to particle number concentration measurements, orders of magnitude difference can exist in aerosol number concentrations, depending on the number and types of sources of particle emissions. Monitoring over several days and during different seasons can provide a better understanding of the variability that might exist in airborne particle number concentrations found in background measurements and in measurements made at sources where manufactured nanomaterials are handled.
- The upper dynamic range of the CPC is 100,000 P/ cm^3. A dilutor, consisting of a modified HEPA filter cartridge placed upstream of the inlet, can extend the range of the CPC when particle number concentrations are greater than 100,000 P/ cm^3 (Peters et al. 2006; Heitbrink et al. 2007; Evans et al. 2008).
- The analysis of air samples by TEM or SEM with energy dispersive X-ray spectrometry can provide information on the elemental composition of the nanomaterials, e.g. NIOSH Method 7402 and 7404 (NIOSH, 1994). However, TEM and SEM analysis can be compromised if there is particle overload on the filter. Alternatively, if the loading is too sparse, an accurate assessment of particle characteristics may not be possible (see 4.3.1).
- Note that area samples are collected as closely as possible to the source of emission to allow for more accurate determination of nanomaterial release and to identify locations most likely to result in worker exposure. Therefore, results from this type of sampling should not be interpreted

as representative of worker exposure. However, samples collected in such a fashion should serve as an indicator of material release and the possible need for controls.

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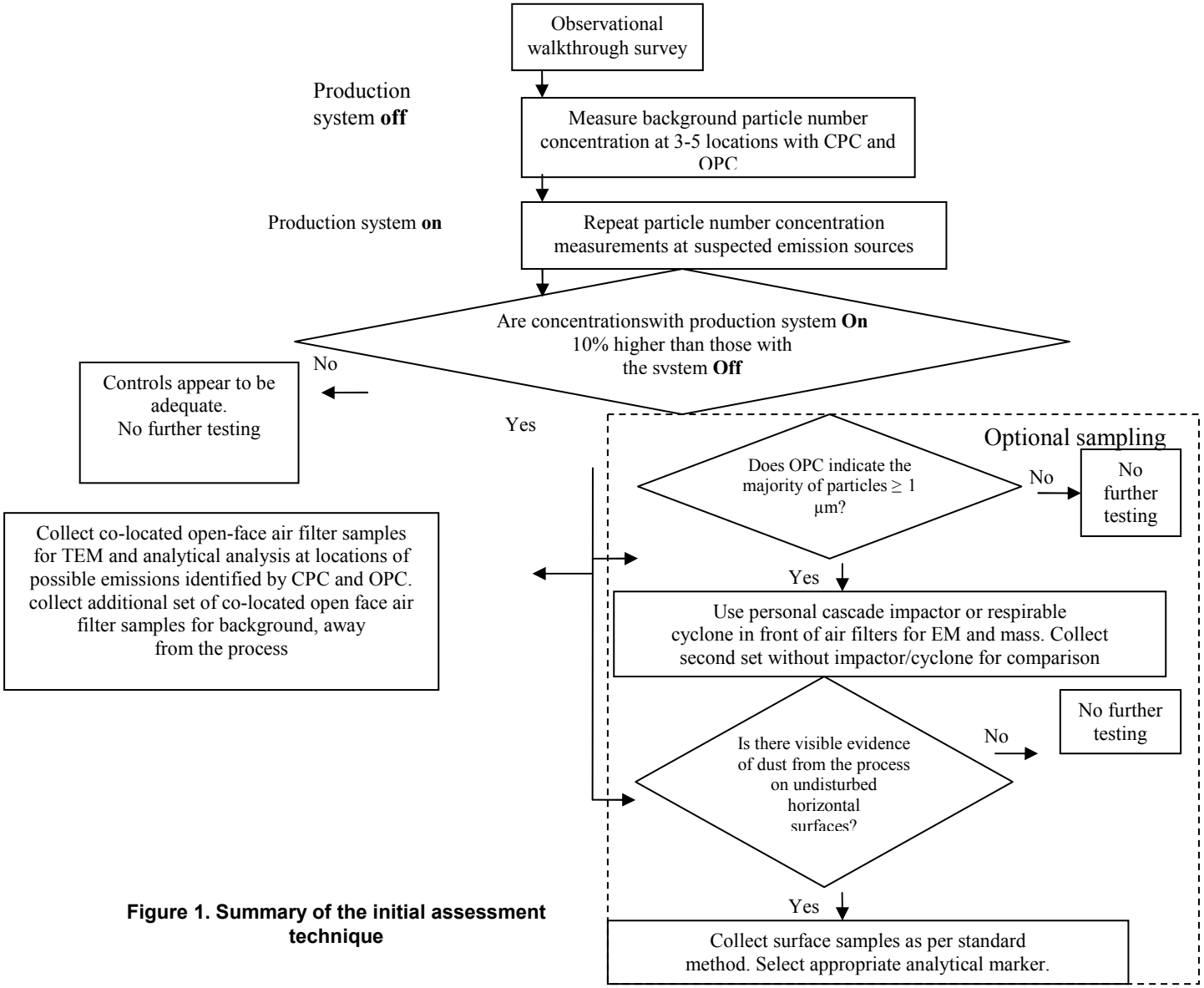

Figure 1. Summary of the initial assessment technique

Figure 2. A demonstration of the initial assessment technique with side by side sampling utilizing OPC, co-located open face filter cassettes and CPC

Table 1 Example of Particle Number Concentration Data Sheet

Date: Facility: Researcher:

Location/ Process/ Task	CPC Particle # 10-1,000 nm (P/cc)	OPC Particle # 0.3 µm (P/Liter)	OPC Particle # 0.5 µm (P/Liter)	OPC Particle # 1.0 µm (P/Liter)	OPC Particle # 10.0 µm (P/Liter)	Possible Measures

Table 2. Approximate sampling times for TEM grid based on particle number concentrations (NIOSH NMAM Method 7402 Asbestos by TEM)

		Open-faced cassettes		
	TEM grid	25-mm	37-mm	47-mm
Diameter (mm)	3.0	25.0	37.0	47.0
Effective Diameter (mm)	3.0	22.2	34.2	44.2
Effective Collection Area (mm^2)	7	385	916	1531
Flow (L/min)	0.1	7	7	7
Desired Loading ($\#/mm^2$)	1.E+06	1.E+06	1.E+06	1.E+06
Air Concentration ($\#/cm^3$)	Time (min)			
250	282.7	220.2	523.4	874.8
500	141.4	110.1	261.7	437.4
1,000	70.7	55.0	130.8	218.7
2,000	35.3	27.5	65.4	109.4
4,000	17.7	13.8	32.7	54.7
8,000	8.8	6.9	16.4	27.3
16,000	4.4	3.4	8.2	13.7
32,000	2.2	1.7	4.1	6.8
64,000	1.1	0.9	2.0	3.4
128,000	0.6	0.4	1.0	1.7
256,000	0.3	0.2	0.5	0.9
512,000	0.1	0.1	0.3	0.4