TECHNICAL SPECIFICATION

ISO/TS 21361

First edition
2019-04

Nanotechnologies — Method to quantify air concentrations of carbon black and amorphous silica in the nanoparticle size range in a mixed dust manufacturing environment

Nanotechnologies — Quantification du noir de carbonne et de la silice amorphe nanométriques en suspension dans l'air en ambiance de production

Reference number
ISO/TS 21361:2019(E)

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Published in Switzerland

Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Nanomaterials are widely used in industrial settings in the manufacture of consumer products. Carbon black and/or amorphous silica are commonly used in consumer products, such as rubber products, insulating materials, and others. Although these materials typically exist as agglomerates in dimensions larger than the nanoscale, there is also potential for worker exposure to these materials in the nanoscale size range. In spite of the widespread use of nanomaterials such as these, quantification of air concentrations of specific nanomaterials in mixed dust settings, such as a manufacturing environment, have been challenging to date and has been identified as a hindrance to the development of nano-specific occupational exposure limits (Gordon, et al. 2014; Hansen, et al. 2012; van Broekhuizen, et al. 2013). This method outlines a technique whereby particles carbon black and amorphous silica can be identified, distinguished, and quantified (in terms of air concentrations) by size in such manufacturing settings. It is anticipated that although this method is specific to carbon black and amorphous silica, the general principles of the method can be applied to many materials in a variety of manufacturing environments. This method advances beyond existing techniques for analysis in that it provides quantitative information regarding exposure to specific materials by size; many other methods provide quantitative information on nanoparticle exposures that are incapable of differentiating by material type. This method includes both a defined methodology for collecting air samples in the manufacturing settings as well as a methodology for analyzing the sample to obtain appropriate information for quantifying air concentration of the materials of interest. Application of this methodology has recently been published in the peer-reviewed literature (Kreider, et al. 2015).

This document will provide guidelines to quantify and identify particles carbon black and/or amorphous silica in air samples collected in a mixed dust industrial manufacturing environment. The guidelines describe air sample collection and the characterization of the particles in the air samples by both particle size and elemental composition. The particles in the air sample are collected in the various stages of a cascade impactor with cut-offs for median particle size between 6 nm and 10 µm. This impactor determines the number particle size distribution in real-time based on the particle aerodynamic diameter. Particles collected on each stage are collected for off-line analysis using Transmission Electron Microscopy (TEM) and Energy Dispersive Spectrometry (EDS) to identify amorphous silica and carbon black particles. The TEM-EDS measurement provides the elemental composition and source of the particles in each stage. Scanning Electron Microscopy (SEM) is also an option to TEM in the electron microscopy/dispersive spectrometry combination. The concentration of particles of a specific nanomaterial in a given size range (#/cm^3) is given by the product of the total particle count for size range (#/cm^3) obtained from the cascade impactor and the fraction of particles identified as the specific material of interest (e.g. carbon black or amorphous silica) from the TEM-EDS results. Though this technique is described for carbon black and amorphous silica, the technique can be applied to the measurement of other particle types, provided they are in the size range of 6 nm to 2,5 µm and can be observed by TEM/SEM and chemically characterized by EDS.

At this time, this methodology represents the one of the methods available to quantify chemical-specific exposures to nanoparticles by size with this degree of sensitivity. Many of the other existing methods that can speciate and quantify chemical exposure in this size range are mass-based, and thus are limited by mass-based detection limits that are high when compared to the mass of particles in this size range. Furthermore, although other sampling methods may be amenable to the techniques described herein, none have been evaluated or validated for this purpose. Therefore, this methodology offers increased sensitivity for quantification of exposure to specific particle types in the nanoscale when such an interest arises. This methodology could be implemented as a higher tier step in an occupational exposure assessment sampling strategy for nanomaterials, particularly in the event hot spots for exposure are identified using other methods and there is an interest in understanding the nature of the exposure. Results from this analysis can be used to compare to health benchmarks, as they become available, to understand potential health risk of workers. In addition, it could be useful in selecting appropriate personal protective equipment (PPE) at a very early stage of the manufacturing process, when required.

Nanotechnologies — Method to quantify air concentrations of carbon black and amorphous silica in the nanoparticle size range in a mixed dust manufacturing environment

1 Scope

This document provides guidelines to quantify and identify air concentration (number of particles/ cm^3) of particles of carbon black and/or amorphous silica by size in air samples collected in a mixed dust industrial manufacturing environment.

The method is defined for air samples collected with an electrical low pressure cascade impactor (ELPCI). on a 25 mm polycarbonate substrate. The method is suitable for sampling in manufacturing environments where there are a variety of particle types contributing to the overall atmosphere. This method is applicable only to environments with chemically and physically distinct particles contributing to aerosols or when confounders can be controlled (e.g. diesel sources). Other sampling methods can also be suitable, though this document is limited to describing methods associated with the electrical low pressure cascade impactor.

Samples collected with the electrical low pressure cascade impactor are analyzed via TEM and EDS to for particle morphology and elemental composition, respectively, to permit identification of particles by type. This information is then used, in conjunction with particle concentration by size range, as determined by the electrical low pressure cascade impactor, to determine concentration of the materials of interest by size.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10312, *Ambient Air — Determination of asbestos fibres — Direct-transfer transmission electron microscopy method*

ISO 4225, *Air quality — General aspects — Vocabulary*

ISO/TS 80004-1, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO 22309, *Microbeam analysis — Quantitative analysis using energy-dispersive spectrometry (EDS) for elements with an atomic number of 11 (Na) or above*

ISO/TS 10798, *Nanotechnologies — Charaterization of single-wall carbon nanotubes using scanning electron microscopy and energy dispersive X-ray spectrometry analysis*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4225 and ISO/TS 80004-1 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
particle aerodynamic diameter
diameter of a sphere of density 1,000 kg m^{-3} that has the same settling velocity as the irregular particle

3.2
cascade impactor
device for simultaneously collecting particles separately in a number of size ranges by impaction, depending on the momentum

3.3
cut-off
size of particles at which the retention efficiency of an instrument device drops below a specified value under defined conditions

3.4
nanoscale
size range from approximately 1 nm to 100 nm

3.5
nanomaterial
material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale

3.6
particle
minute piece of matter with defined physical boundaries

3.7
sampling time
interval of time over which a single sample is taken

4 Principle

Air sampling is conducted using an electrical low pressure cascade impactor (ELPCI). The ELPCI is a cascade impactor with multiple stages representing different size bins, distinguished based on aerodynamic diameter. The cascade impactor is connected to a vacuum pump, which pulls air (and subsequently airborne particles) into the impactor. As particles enter the cascade impactor, they are charged and then subsequently separated by aerodynamic size onto different stages. As the particles come into contact with the surface of their appropriate stage, they transmit an electrical current to the ELPCI. This electrical current is then converted into a particle count for that stage, thus permitting the ELPCI to conduct real-time particle counting. This particle count is reported as number of particles per cm^3 of air. In addition to the particle counting function, the ELPCI also allows for collection of samples on each stage, using a 25 mm polycarbonate substrate.

Following completion of air sampling, these substrates are analyzed via TEM to identify the particles on each stage by morphology coupled with EDS to identify the particles on each stage by elemental composition. A minimum of 100 distinct particles per stage are analyzed using TEM- EDS to identify the particle type, based on the chemical signature of the particles. Carbon black, made up primarily of elemental carbon, elicits a strong carbon signal (and absence of other signals) on the EDS, whereas silica (SiO_2) elicits a strong silicon and oxygen signal. These profiles are used to designate particles as carbon black or amorphous silica. Where there are potential confounders present in the sample, such as soot (for carbon black) or crystalline silica (for amorphous silica), particle morphology and/or diffraction pattern must be relied upon to identify the particles. Morphology is the main attribute that distinguishes carbon black from soot, whereas morphology and diffraction can be used to distinguish crystalline silica from amorphous. Furthermore, comparison to the morphology of the source materials (e.g. carbon black or amorphous silica) can be evaluated under TEM to ensure appropriate assignation of the particle type. The relative proportion of particles (e.g. number of particles by type out of 100 total particles identified per size fraction) identified by type of particle (carbon black, amorphous silica, or other) is the key outcome of this analysis.

To determine air concentration of the materials of interest (e.g. carbon black or amorphous silica), the proportion of particles identified by type is multiplied by the total number of particles in each size bin determined during the real-time air sampling. The outcome of this analysis is the air concentration of each material type by size in number of particles/cm^3.

Though the method described herein will specifically focus on the analysis of carbon black and amorphous silica, this methodology is transferrable to other materials, provided they have a unique signal under EDS and/or are distinguishable via morphology under TEM.

5 Abbreviations

EDS energy dispersive spectroscopy

ELPCI electrical low pressure cascade impactor

HEPA high efficiency particulate arrestance

LOD limit of detection

PM10 airborne particles with an aerodynamic diameter less than 10 µm

SEM scanning electron microscopy

TEM transmission electron microscopy

6 Reagents

During the analysis, use only reagents of recognized analytical grade. All agents listed are required to execute the transfer of the polycarbonate substrate content onto a TEM grid in accordance with ISO 10312. No additional reagents are required for execution of this specification.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

6.1 Water, fibre-free.

A supply of freshly distilled, fibre-free water, or another source of fibre-free, pyrogen-free water shall be used.

6.2 Chloroform, analytical grade.

Distilled in glass, preserved with 1 % (WV) ethanol; used to dissolve polycarbonate substrate.

6.3 l-Methyl-2-pyrrolidone.

Used to dissolve polycarbonate substrate.

6.4 Dimethylformamide.

Used to dissolve polycarbonate substrate.

6.5 Glacial acetic acid.

Used to dissolve polycarbonate substrate.

6.6 Acetone.

Used to dissolve polycarbonate substrate.

7 Apparatus

7.1 Air sampling — Equipment and consumable supplies

7.1.1 Electrical low cascade pressure impactor (ELPCI)

An electrical low pressure cascade impactor, consisting of a minimum of 14 size bins, should be used for collection of air samples. Of the size bins, at least 3 should be within the nanoscale, defined as less than 100 nm. The ELPCI should be operated in accordance with the manufacturer's instructions.

An example of measurement capability for a commercially available electrical low pressure impactor operating at a 10 l/min flow rate is presented in the Table 1.

Table 1 — Measurement range for commercially available electrical low pressure cascade impactor (Dekati, 2011)

D50 % nm	Di nm	Number min 1/cm³	Number max 1/cm³	Mass conc. min µg/m³	Mass conc. max µg/m³
10 000	Unavailable	Unavailable	Unavailable	Unavailable	Unavailable
6 800	8 200	0,1	2,40E+04	30	10 000
4 400	5 500	0,1	2,40E+04	10	3 000
2 500	3 300	0,15	5,40E+04	3	1 000
1 600	2 000	0,3	1,10E+05	1,4	450
1 000	1 300	0,5	1,90E+05	0,7	210
640	800	1	3,50E+05	0,3	100
400	510	2	6,40E+05	0,1	50
260	320	3	1,20E+06	0,07	20
170	210	5	2,10E+06	0,03	10
108	140	10	3,70E+06	0,02	5
60	80	20	7,30E+06	0,005	2
30	42	50	1,70E+07	0,002	0,5
17	22	100	3,40E+07	0,001	0,25
6	1	250	8,30+07	0,000 4	0,13
D50 % = Aerodynamic diameter cut-offs for 50 % efficiency; Di = Geometric mean aerodynamic diameter of stage					

7.1.2 Limit of Detection

Based on the table above and the expected volumetric flow rate of the sampling equipment (10 l/min), the practical limits of detection (LOD) for both carbon black and amorphous silica (based on a one-second sample) by particle size are found in Table 2.

Table 2 — Limits of detection by particle size (Dekati, 2011)

D50 % nm	Di nm	LOD in # of particles
10 000	Not applicable	
6 800	8 200	16,6
4 400	5 500	16,6
2 500	3 300	24,9
D50 % = Aerodynamic diameter cut-offs for 50 % efficiency; D_i = Geometric mean aerodynamic diameter of stage; LOD = Limit of detection.		

Table 2 *(continued)*

D50 % nm	Di nm	LOD in # of particles
1 600	2 000	49,8
1 000	1 300	83
640	800	166
400	510	332
260	320	498
170	210	830
108	140	1 660
60	80	3 320
30	42	8 300
17	22	16 600
6	1	41 500
D50 % = Aerodynamic diameter cut-offs for 50 % efficiency; D_i = Geometric mean aerodynamic diameter of stage; LOD = Limit of detection.		

Detection limits presented in this table are approximate based on a typical impactor; each impactor has exact specifications that may result in deviations from the reported detection limits. The detection limit for a specific duration can be calculated by converting the minimum concentration of particles detectable to number of particles based on sample duration and volumetric flow rate of the impactor. Increasing the duration of sampling will decrease the detection limit based on increased volume of collection.

7.1.3 Real-time aerosol monitor

A real-time aerosol monitor, capable of measuring mass of particulate consistent with the size range of the ELPCI (e.g. PM10 if largest size bin of ELPCI is 10 µm), should be operating coincident with the ELPCI sampling. Output of the real-time aerosol monitor will be used to appropriately designate sample time of the ELPCI to prevent under/overloading of the substrate (see 8.2 and Table 3). The real-time aerosol monitor should be operated in accordance with the manufacturer's instructions.

7.1.4 Vacuum pump

A vacuum pump, calibrated to a flow rate consistent with what is required for appropriate size fractionation in the ELPCI (i.e. 10 l/min), will be required to introduce air and particles into the cascade impactor. The vacuum pump should be operated in accordance with the manufacturer's instructions.

7.1.5 Polycarbonate substrate

A 25-mm polycarbonate substrate. The substrate should be compatible with the stages of the ELPCI. Polycarbonate substrates should be handled using tweezers or similar to prevent transfer of oils from the skin. This polycarbonate substrate is mounted in the ELPCI for sample collection.

Other collection media, such as polycarbonate filters, mixed cellulose ester filters, or others, could be considered only if and when proper steps are taken to ensure size fractionation is unaffected by the selected media.

7.1.6 Hydrocarbon grease

A silicone- and halogen-free vacuum grease is recommended for use on the surface of the selected stages to prevent particle bounce within the cascade impactor. Select stages will be treated with this grease at the time of sampling.