



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review of measurement techniques and methods for assessing personal exposure to airborne nanomaterials in workplaces

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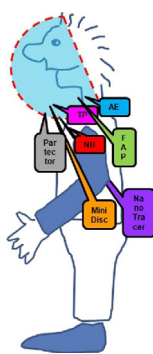
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HIGHLIGHTS

- Personal samplers and monitors are robust and ready for field-use.
- Typical accuracy of personal samplers and monitors around $\pm 30\%$
- Combination of personal sampler and monitor may be the optimal choice.
- Clear measurement strategy needed for assessing personal exposure

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 November 2016

Received in revised form 21 February 2017

Accepted 6 March 2017

Available online xxx

Keywords:

Personal exposure
Nanomaterials
Personal sampler
Personal monitor
Exposure assessment

ABSTRACT

Exposure to airborne agents needs to be assessed in the personal breathing zone by the use of personal measurement equipment. Specific measurement devices for assessing personal exposure to airborne nanomaterials have only become available in the recent years. They can be differentiated into direct-reading personal monitors and personal samplers that collect the airborne nanomaterials for subsequent analyses. This article presents a review of the available personal monitors and samplers and summarizes the available literature regarding their accuracy, comparability and field applicability. Due to the novelty of the instruments, the number of published studies is still relatively low. Where applicable, literature data is therefore complemented with published and unpublished results from the recently finished nanoIndEx project. The presented data show that the samplers and monitors are robust and ready for field use with sufficient accuracy and comparability. However, several limitations apply, e.g. regarding the particle size range of the personal monitors and their in general lower accuracy and comparability compared with their stationary counterparts.

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The decision whether a personal monitor or a personal sampler shall be preferred depends strongly on the question to tackle. In many cases, a combination of a personal monitor and a personal sampler may be the best choice to obtain conclusive results.

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1. Introduction

The use of manufactured nanomaterials (MNMs) has increased at a constant pace over the recent years. Their applications range from scratch resistant surface coatings (Bauer et al., 2006) or lotus-leaf-like self-cleaning textiles (Liu et al., 2007), via building materials (Pacheco-Torgal and Jalali, 2011), energy applications (Arico et al., 2005) and enforced polymers, e.g. for dental applications (Hannig and Hannig, 2010), to enhanced cosmetics (Bowman et al., 2010). Besides the tremendous new opportunities offered by these novel materials, concerns have been raised because of potential adverse health effects that may arise if MNMs are taken up by the human body (Oberdörster, 2000; Simkó and Mattsson, 2010; Hoet et al., 2004; Gwinn and Vallyathan, 1818; Madl and Pinkerton, 2009). While human exposure to MNMs may in principle occur during any stage of the material's lifecycle (Hischier and Walser, 2012), it is most likely in workplaces where these materials are produced or handled in large quantities or over long periods of time (Kuhlbusch et al., 2011). Inhalation is considered as the most critical uptake route (Wiesner et al., 2006), because the small particles are able to penetrate deep into the lung and deposit in the gas exchange region. Inhalation exposure to airborne MNMs therefore needs to be assessed in view of worker protection.

Exposure to airborne agents can generally best be assessed by measuring the individual exposure in the personal breathing zone (PBZ) of an individual. The PBZ is defined as a 30 cm hemisphere around mouth and nose (EN, 2012). Measurements in the PBZ require instruments that are small and lightweight. The individual exposure specifically to MNMs has not been assessable in the past due to the lack of suitable personal samplers and/or monitors. Instead, most studies related to exposure to MNMs have been carried out using either bulky static measurement equipment or not nanospecific personal samplers (Kuhlbusch et al., 2011; Brouwer et al., 2004). In recent years, novel samplers and monitors have been developed that allow for an assessment of the more nanospecific personal exposure to airborne MNMs. In the terminology used here, *samplers* are devices that collect particles onto a substrate, e.g. a filter or flat surface, for subsequent analysis, whereas *monitors* are real-time instruments that deliver information on the airborne concentrations with high time resolution. Only a few of these samplers and monitors are commercially available and are reviewed here regarding their comparability, accuracy and field usability. Where applicable, information from the scientific literature is accompanied with data obtained within the nanoIndEx project (project period June 1st, 2013–May 30th, 2016).

Besides personal samplers and monitors, (personal) exposure measurements require a clear strategy (Brouwer et al., 1867; Asbach et al., 2014). The exact strategy can vary depending on the local settings in the workplace and may need to be tailored to the questions to be tackled. The choice of instruments is affected by the measurement strategy. If, for example, task based exposure with short-lived spikes in the concentrations is to be assessed, the use of personal monitors with high time resolution is required. In contrast, for the determination of (e.g. shift-based) average concentrations, samplers may also be used. If personal exposure to a certain chemical species shall be assessed, then with the currently available technology, this can only be achieved by particle sampling and subsequent chemical analysis of the deposit. Placement of the instruments for monitoring of the background or far field concentrations is also an important component of the measurement strategy.

This article presents the state of the art in personal exposure assessment for nanomaterials. While the focus of this paper is on exposure to manufactured nanomaterials in workplaces, most findings are also directly applicable to the assessment of exposure to non-engineered nanoscale particles, e.g. in the environment (Asbach and Todea, 2016).

2. Review of measurement and sampling techniques for personal exposure assessment

Personal exposure measurement requires the use of personal samplers and monitors (Koehler and Peters, 2015). The requirements for an instrument to be considered a personal monitor or sampler are a small size, low weight and a possibility for battery operation. The size and weight of a personal instrument should be small enough to be mounted directly within the PBZ of the individual. Alternatively, larger instruments can be mounted on a belt and sample from the PBZ through flexible tubes. The battery lifetime should ideally be ≥ 8 h, so that the instrument can be used for the duration of a full work shift.

Several prototype samplers (Azong-Wara et al., 2009; Azong-Wara et al., 2013; Furuuchi et al., 2010; Thongyen et al., 2015; Tsai et al., 2012; Zhou et al., 2014; Chen et al., 1999) and monitors (Wasisto et al., 2015; Qi et al., 2008; Liu and Chen, 2016; Li et al., 2009a) have been developed over the last years, however, only those that are commercially available and/or are used routinely are described here.

2.1. Metrics issues

Currently, with very few exceptions, no occupational exposure limits specifically for MNMs are available and instead the conventional mass concentration limits apply for chemicals and dusts. However, in this regard it is important to note that even if the number concentration is often dominated by nanoscale particles, such as MNMs, their mass is usually negligible compared to that of coarse particles. Consequently, other metrics than mass may need to be taken into account in order to make an adequate and comprehensive evaluation of exposures to MNMs in workplaces. Unfortunately, it is not yet clear which key particulate parameters (mass, surface area, number concentration or their size distributions) could be the most relevant measurement unit with regard to MNM-related (occupational) health effects (Wittmaack, 2007; Rushton et al., 2010). While traditionally the particle mass concentration of airborne particles has been determined as exposure metric, other studies have shown that the particle number concentration (Peters et al., 1997) or the surface area concentration (Oberdörster, 2000; Driscoll, 1996; Schmid and Stoeger, 2016) may be better predictors for the health outcomes. However, Sager and Castranova (2009) reported that surface area alone may not be a sufficient health effect indicator, as in their study ultrafine titanium dioxide showed a higher bioactivity than carbon black for the same surface area dose. As of now, no instrument exists that is capable of measuring the geometric surface area of airborne particles. The only surface area related metric that can be determined for airborne particles is the so-called lung deposited surface area (LDSA) concentration, i.e. the fraction of the airborne surface area concentration that would deposit in the alveolar region of the human airways. To estimate the lung deposition, the physiological and breathing data for a reference worker are considered (Fissan et al., 2007). The LDSA concentration is measured by electrically charging aerosol particles with a unipolar diffusion charger, followed by a measurement of the current induced by charged particles. The

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