Assessment of personal exposure to airborne nanomaterials: Evaluation of a novel sampler

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Abstract. A novel sampler, the NANOBADGE, has been developed to assess personal exposure to nano-objects, agglomerates and aggregates (NOAA) at the workplace. The NANOBADGE collects particles on filters subsequently analyzed by X-Ray Fluorescence spectroscopy (XRF), which provides a mass-based quantification with chemical selectivity. The NANOBADGE was benchmarked against a scanning mobility particle sizer (SMPS) and a DiSCmini by carrying out simultaneous measurements on test aerosols of ZnO or TiO$_2$ for particle sizes between 20 and 400 nm for which the DiSCmini has its highest accuracy. The effective density and shape of the NOAA present in the test aerosols were determined experimentally to compare number-based data obtained with the SMPS and the DiSCmini with mass-based data obtained with the NANOBADGE. The agreement between the SMPS and the NANOBADGE sampler was within ± 25 % on all test aerosols. The converted DiSCmini data matched the SMPS and sampler data for polydisperse aerosols in the specified size range as long as the DiSCmini assumptions meet the aerosol characteristics (i.e. lognormal size distribution with a given geometric standard deviation $\sigma_g = 1.9$). The detection limits of the NANOBADGE sampler were in the order of tens of nanograms per filter, which is low enough to reliably detect exposure levels below the recommended exposure limit (REL) of the National Institute for Occupational Safety and Health (NIOSH) and the Institut National de Recherche et de Sécurité (INRS) for ultrafine ZnO and TiO$_2$ even for short-term exposure situations.

1. Introduction
The manufacturing and use of engineered nano-objects, agglomerates and aggregates (NOAA) has increased rapidly over the recent years. NOAA are now mass-produced, used for a very wide range of applications and incorporated into mainstream consumer products [1]. Besides the obvious benefits these materials bring, their potential adverse health and environmental effects, particularly caused by inhalation, are raising growing concerns [2-4]. The intrinsic ability of NOAA to reach and deposit in the deep alveolar region of the lungs suggests that their toxicity and fate may differ significantly depending on the particle size, shape and chemical composition [5, 6]. Although the likelihood for exposure to NOAA by inhalation is higher for workers producing or handling these products at the industrial scale, end-users are also potentially exposed and the airborne release of NOAA in the environment cannot be excluded [7-9]. Since the hazards and the
environmental impact are unknown, precautionary safety measures in the nanomaterial industry should ideally involve a continuous tracking of the personal exposure to airborne NOAA [10].

There is no scientific agreement on the best metric for exposure assessment between number, surface area or mass concentration [11]. With the exception of fibers which are counted by number, mass concentration remains the most widespread metric [12, 13]. Most published studies on inhalation exposure used stationary measurement equipment [14, 15]. Although several personal samplers and monitors became available lately [16-20], the number of studies on their comparability and accuracy is still rather low [21-24]. Within the framework of the nanoIndEx project, we propose to evaluate herein the performance of the NANOBADGE personal sampler.

![Figure 1. Picture of the NANOBADGE personal sampler equipped with a filter cartridge.](image)

The NANOBADGE sampler is a battery-operated portable device which collects airborne particles in the breathing zone of the worker, defined as a 30-cm hemisphere around mouth and nose [25]. The device has been designed to minimize the burden in terms of weight and noise and is operated with a single button, as shown in Figure 1 [26]. The sampler is connected to filtration cartridges, whose filters are then analyzed offline by X-Ray Fluorescence spectroscopy (XRF). This highly-sensitive technique yields the elemental composition of the collected particles with sensitivity in the order of a few tens of nanograms per filter. Moreover it is a non-destructive analytical technique, meaning that the same sample can be characterized with other techniques such as scanning electron microscopy [5]. The sampler can be equipped with a pre-separator with a cut-off diameter of 4 µm to remove coarse particles.

The sampler was compared to a stationary instrument, the scanning mobility particle sizer (SMPS), and to a personal monitor, the DiSCmini [17, 24, 27]. A procedure has been developed to compare the number-based metrics of the SMPS and the DiSCmini to the mass-based value obtained with the sampler. For that purpose, aerosols with particle sizes within 20-400 nm were used since the comparability of personal monitors and SMPS on the mean particle size and number concentration are respectively within ± 30% and ± 50% in this specified size range [28]. The performance and the ability of the NANOBADGE to perform personal exposure measurements to airborne nanomaterials will be discussed.

2. Materials and methods
The DiSCmini is equipped with an impactor with a cut-off at around 700 nm to remove coarse particles which cannot be sized correctly by the monitor [17]. In order to test the instruments under the same conditions, during all tests with monodisperse and polydisperse aerosols in the 20-400 nm size range the
tested NANOBADGE and DiSCmini were run without the use of a pre-separator. This is not detrimental for the performance of the instruments as the modal diameter of the test aerosols was much smaller than the cut-off of their impactors. The NANOBADGE sampler (2013 version operated with a flowrate of 0.6 L/min) was equipped with polycarbonate filters (Whatman® Nuclepore Track-Etched Membranes, pore size 0.4 µm) for the collection of particles. The filters were analyzed by XRF, providing a cumulative mass-based quantification of the chemical elements present on the filters. Thus, the sampler provided the mass concentration in the personal breathing zone averaged over the total sampling time.

The XRF analysis was performed on a Rigaku Nanohunter XRF spectrometer operating at 50 kV, 0.80 mA, equipped with copper and molybdenum anodes. The former anode was chosen to detect and to quantify titanium, and the latter for zinc. The Z-offset (vertical position of the upper surface of the sample with respect to the excitation beam) has been optimized for every measurement in order to get fluorescence signal from the filter only, based on the intensity of the element which was considered (Ti or Zn). An acquisition time of 200 s and an incident angle of 0.75° were used. The fluorescence intensity of the element has been normalized by the area of the inelastic scattering peak (16.5-18 keV) for the molybdenum anode and by the area of the inelastic and elastic scattering peak (7.71-8.40 keV) for the copper anode [29-31]. The quantification by mass of the elements deposited on the filters required that the XRF spectrometer is calibrated, which was done using a previously reported methodology [32]. In short, sets of filters of increasing particle loading were generated by sampling aerosols of ZnO or TiO$_2$. The filters were then analyzed by XRF, followed by dissolution of the particles for elemental quantification by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The detailed procedure is described in the Supplementary Material. The plot of the normalized XRF intensity versus the mass determined by ICP-MS lead to the calibration curves for Ti and Zn, used to convert the X-ray fluorescence intensity to mass. For comparison of the mass with the SMPS and DiSCmini data, we assumed that the elements detected were present as oxides.

The limit of detection (LOD) was estimated for ZnO and TiO$_2$ from the measured XRF intensity on 3 blank filters. For each filter, the minimum detectable intensity $I_{LOD}$ was calculated from the mean normalized intensity $<I>$ of the element considered and the standard deviation $\sigma$ of 5 independent measurements [33]:

$$I_{LOD} = <I> + 4.65\sigma$$ (1)

This minimum detectable intensity was converted to a minimum detectable mass using the calibration curve.

Simultaneous samplings with the SMPS, the DiSCmini and the NANOBADGE sampler were carried out using the experimental setup shown in Scheme 1. The test aerosols of ZnO and TiO$_2$ were generated by atomization of aqueous dispersions (200 mg/L and 100 mg/L in water for ZnO and TiO$_2$, respectively). The dispersions were prepared by dilution of concentrated stock dispersions with ultrapure water (Milli-Q, Millipore, Billerica, USA): a commercial ZnO dispersion (Evonik “VP Disp ZnO 20 DW”, 35 wt% in water) and a TiO$_2$ dispersion (TiO$_2$ anatase, Nanostructured & Amorphous Materials Inc., 5-30 nm APS, 15 wt% in water). A TSI aerosol generator (TSI model 3076) was used to produce the aerosols, dried with a silica gel diffusion dryer (TSI model 3062). Polydisperse aerosols were introduced through an aerosol neutralizer ($^{85}$Kr source, 74 MBq) into a vertical chamber (ca. 120 cm high, inner diameter 29 cm) in a laminar flow (30 L/min, Re=20) of HEPA (high-efficiency particulate arrestance)-filtered dilution air. In order to study monodisperse test aerosols, a differential mobility analyzer (DMA - TSI long model 3081, sheath air 5 L/min, aerosol flowrate 1 L/min) was added between the atomizer and the vertical chamber. The NANOBADGE sampler and the DiSCmini monitor were installed inside the tunnel, along with a thin-walled sampling probe connected to a SMPS (TSI model 3080 with a DMA from TSI, model 3081, sheath air 5 L/min, aerosol flowrate 1 L/min) was added between the atomizer and the vertical chamber.
3 L/min). The uniformity in space of the particle number concentrations was checked in the sampling area of the chamber (see Supplementary Material).

Scheme 1. Experimental setup used for the generation and simultaneous sampling and monitoring of the monodisperse aerosols. The DMA was by-passed when sampling polydisperse aerosols. Adapted from Trakumas and Salter [34].

The comparison between the mass concentration determined by XRF with number-based data from the SMPS and the DiSCmini required knowledge of the effective densities of the particles. The effective density is defined as the mass of a particle divided by the volume of a spherical particle having the same mobility diameter. It is determined by comparing the mobility diameter, which is independent of particle mass, with the aerodynamic diameter. The effective density of the generated NOAA was estimated using a DMA coupled to an Electrical Low-Pressure Impactor (ELPI)[35]. Polydisperse aerosols of the particles of interest were first classified by a DMA (TSI long model 3081, sheath air 10 L/min) around a set mobility diameter before entering the ELPI for aerodynamic sizing, as shown in Scheme 2. The ELPI was provided with 1 L/min of the size-classified aerosol complemented by 9 L/min of HEPA-filtered air. The mobility diameter was chosen as the modal diameter of the polydisperse aerosol to get sufficiently high aerosol concentrations after size classification.
Scheme 2. Tandem DMA-ELPI set-up for the determination of the effective density.

The effective density $\rho_{\text{eff}}$ was calculated from the mobility diameter $d_m$ and the aerodynamic diameter $d_a$ as:

$$\rho_{\text{eff}}(d_m) = \frac{\rho_0 c_e(d_m) d_a^2}{c_e(d_m) d_m^2},$$  \hspace{1cm} (2)

where $\rho_0 = 1 \text{ g/cm}^3$.

The Cunningham slip correction

$$C_c(d) = 1 + \frac{\lambda}{d} \left( 2.284 + 1.116 \exp\left(-\frac{0.5d}{\lambda}\right) \right),$$  \hspace{1cm} (3)

and the mean free path $\lambda = 0.066 \mu\text{m}$ [36, 37].

The mean aerodynamic diameter $d_a$ was calculated from the currents and the cut-point diameters of the ELPI impactor stages.

$$d_a = \exp\left( \frac{\sum_i l_i \ln d_i}{\sum_i l_i} \right)$$  \hspace{1cm} (4)

In order to compare the quantification by mass of the sampler with number-based metrics provided by the SMPS and the DiSCmini, the particles in the aerosol were assumed to be spherical. The shape of the sampled NOAA was assessed by Scanning Electron Microscopy [5] using a LEO 1530 instrument (LEO Electron Microscopy Ltd, Cambridge, England, acceleration voltage 10 kV, in-lens detector). The polycarbonate filters were coated with platinum to mitigate charging effects.

For the SMPS, the total mass per unit volume of air (g/cm$^3$) was calculated by summation of the number concentrations for each size channel according to:

$$m = \rho_{\text{eff}} \sum_{D_p=14.6 \text{ nm}}^{D_p=661.2 \text{ nm}} \frac{\pi D_p^2 N_p(D_p)}{6} dD_p$$  \hspace{1cm} (5)

where $D_p$ is the mobility diameter [35], $N_p(D_p)$ is the number concentration of particles having the mobility $D_p$ (cm$^3$) and $\rho_{\text{eff}}$ is the effective density (g/cm$^3$). The expected mass collected by the sampler can be determined from the sampling flowrate and duration.
For the DiSCmini, we have used the built-in mass concentration provided by the software (Datatool v1.217). The calculation is based on the Hatch-Choate equations [37], which are used to convert the count mean diameter to volume mean diameter:

\[ m = \rho N \frac{\pi}{6} d^3 e^{4.5(n \sigma)^2}, \]  

where \( N \) is the total particle concentration by number and \( d \) is the mean particle size determined by the DiSCmini. The calculation is only valid for polydisperse aerosols having a lognormal size distribution. The software uses a geometric standard deviation \( \sigma \) of 1.9 and a density of \( \rho \) of 1.2 g/cm\(^3\) by default [38]. Therefore, experiments made with aerosols that differ significantly from the assumptions made should be analyzed carefully since they might lead to erroneous results. We have scaled the obtained value according to the measured effective density \( \rho_{eff} \) for comparison with the sampler.

### 3. Results and Discussion

The effective densities of ZnO and TiO\(_2\) aerosols were determined using the DMA-ELPI tandem setup shown in Scheme 2. For each aerosol, the electrical mobility diameter of the DMA was matched to the largest modal diameter of the aerosol, which depends on the type of powder and the concentration of the dispersion. The resulting values for the effective density are given in Table 1. The effective densities determined for the NOAA of ZnO and TiO\(_2\) corresponded to approximately 40% of the values for bulk materials. In both cases the packing density of the NOAA was similar, which was confirmed visually on the SEM images in Figure 2. In addition, the shape of the NOAA was nearly spherical. Thus the assumption of spherical particles made to calculate the mass from the SMPS and the DiSCmini data was expected to be reasonable.

**Table 1.** Effective density calculated for the aerosols generated by atomization. The effective density of bulk ZnO and TiO\(_2\) is 5.61 g/cm\(^3\) and 3.9 g/cm\(^3\), respectively. The uncertainty on the density was calculated as twice the relative standard deviation of 100 measurements.

| Material | Concentration (mg/L) | Selected mobility diameter [9] | Average aerodynamic diameter [9] | Density (g/cm\(^3\)) | Uncertainty |
|----------|-----------------------|-------------------------------|-------------------------------|-----------------------|-------------|
| ZnO      | 200                   | 100                           | 181                           | 2.2 ± 2 %            |             |
| TiO\(_2\) | 100                   | 60                            | 79                            | 1.4 ± 4 %            |             |

**Figure 2.** SEM images of the polycarbonate filters exposed to ZnO (a) or TiO\(_2\) (b) NOAA generated by atomization.
The SMPS and the NANOBADGE sampler have been compared on three monodisperse ZnO aerosols which were classified at 75, 100, and 200 nm using a DMA (Scheme 1). The error bars for the SMPS were calculated as twice the average standard deviation of the total number concentration. A value of 20 % was obtained, in good agreement with previous literature [27]. Considering that the error on the density is within 5 %, an accuracy of ± 25 % was used for the SMPS data. A relative error of 10 % on the mass measured by XRF was estimated, due to the calibration procedure and the regulation of the sampling flowrate (more details are given in the supplementary information). As shown in Figure 3, the agreement between the mass calculated from the SMPS and the mass measured by XRF is good. It is worth mentioning that the properties of the test aerosols are ideal for the purpose of this study, since the NOAA are monodisperse, nearly-spherical and in the 20-400 nm size range recommended for the highest accuracy of the DiSCmini.

![Figure 3](image)

**Figure 3.** Mass of ZnO calculated from the SMPS data and mass of ZnO measured by XRF analysis of the NANOBADGE filters (calculated from the mass of Zn). An effective density of 2.2 was used.

The DiSCmini portable monitor was compared with the SMPS and the NANOBADGE sampler for test aerosols of ZnO (monodisperse aerosol classified at 200 nm) and TiO$_2$ (polydisperse aerosol with a geometric mean diameter of 60 nm and standard deviation of 1.8). The results are reported in Figure 4. The accuracy for the SMPS and the NANOBADGE was calculated as described above for ZnO. For the DiSCmini, the accuracy on the mass was estimated as twice the average standard deviation of the number concentration (± 30 %), in good agreement with previously reported values [21, 24]. The uncertainty on the density (± 5 %) was added for a total accuracy of ± 35 %.

All three instruments yielded comparable results on the polydisperse TiO$_2$ aerosol despite the slight difference regarding the measured geometric standard deviation of the aerosol size distribution (1.8 vs the 1.9 value used by the DiSCmini). However, for the monodisperse ZnO aerosol, the DiSCmini overestimated the mass. This significant deviation originates from assumptions for the aerosol size distribution in the DiSCmini: a lognormal size distribution with a geometric standard deviation of 1.9 is used to calibrate the device response and to convert the data to mass [38, 39]. The monodisperse ZnO aerosol has a narrow size-distribution ($\sigma = 1.3$, see Supplementary Material), which results in errors on the particle number concentration and the mean particle size recorded by the DiSCmini. The document “miniDiSC application note 11” provides correction factors for aerosols that do not match the assumed size distribution. The contour plot of the simulated particle number response indicates that the DiSCmini underestimates the number
concentration by 15%, leading to an underestimation of the mass by the same amount. In addition the DiSCmini underestimates the particle size by 5%, leading to an underestimation of the sampled mass by 15.8%. The last correction consists in using the measured σ in Equation 6. This calculation shows that the mass was overestimated by a factor of 4.7. Combining these three corrections, a direct use of the DiSCmini data overestimated the mass by a factor of 3.4. Thus the true mass should be 19.7 µg/m³ which is close to a factor of 2 to the SMPS and NANOBADGE results and not a factor of 7.

The DiSCmini has its highest accuracy for particle sizes between 20 and 400 nm, with an optimum around 100 nm [17, 22, 24]. The properties of the TiO₂ polydisperse aerosol were much more suitable for the DiSCmini, with a mean particle size (60 nm) and geometric standard deviation (1.8) which are close to the assumptions of the device software. Corrections to compensate the slight deviation of σ indicates that the DiSCmini does not affect the particle number response while it underestimates the particle size by 5%. Moreover, the wrong σ used in Equation 6 involves an overestimation of the mass by a factor of 1.35 which consequently implies an overall overestimation of the mass by a factor of 1.157. This overestimation by 13.6% stay in the ± 30 % accuracy margin. Therefore, one can say that in this case all three instruments yielded similar results for the mass.

When the aerosol features deviated from the ideal values (in particular when classified aerosols were studied), the direct use of the DiSCmini data and its conversion tool should be taken with caution unless it can be confirmed by some other method.

![Figure 4](image_url)

**Figure 4.** Mass of ZnO and TiO₂ collected on the filters, calculated from the SMPS and the DiSCmini data and measured by XRF for the NANOBADGE sampler. Effective densities of 2.2 and 1.4 were used for ZnO and TiO₂, respectively. *The mass of ZnO calculated from the DiSCmini data was significantly overestimated by using a wrong assumption on the geometric standard deviation of the aerosol. By applying corrections, the mass recalculated from DiSCmini data was 19.7 µg/m³ and not 67.4 µg/m³ as shown in the figure. Based on those calculations, the true mass is close to a factor of 2 to the SMPS and NANOBADGE results and not a factor of 7 as it was initially the case.*
To further illustrate the validity of the sampler for personal exposure assessments, the LOD for ZnO and TiO₂ were determined. The European Agency for Safety and Health at Work distinguishes long-term and acute exposure, the former being a repeated exposure averaged over working shifts of 8 h and the latter a peak exposure averaged over 15 min [40]. Thus the LOD had been converted to aerosol mass concentrations for a full shift based on the latest recommended exposure levels (REL) of the National Institute for Occupational Safety and Health (NIOSH) [13, 41, 42]. The minimum sampling time required to detect an exposure at or above the REL was also calculated. As shown in Table 2, the limits of detection are much lower than the REL for the two oxides considered in this study. The detection of peak exposure is also possible, since few seconds of sampling at or above the REL are sufficient to exceed the LOD. Since the LOD are several orders of magnitude smaller than the current REL, the NANOBADGE sampler can already accommodate tougher regulation, should the exposure levels be lowered in the future.

### Table 2. Comparison between the recommended exposure levels (REL) published by the NIOSH and the limits of detection (LOD) of the NANOBADGE sampler for shift and acute exposure (NIOSH, 2007, 2009).

| REL for ultrafine dust from NIOSH (µg/m³) | LOD (ng/filter) | LOD (µg/m³) for 8 h of sampling | Minimum sampling time at the REL |
|-------------------------------------------|-----------------|---------------------------------|---------------------------------|
| ZnO                                       | 5000            | 30 ± 20 %                       | 0.1 ± 25 %                     | < 1 min                      |
| TiO₂                                      | 300             | 12 ± 25 %                       | 0.04 ± 30 %                    | < 1 min                      |

### 4. Conclusion

A novel sampler to assess personal exposure to NOAA was developed, based on the collection of particles on filters followed by elemental analysis by XRF. This analysis yields an integrated mass-based exposure value for the chemical elements of interest. In order to assess the validity of the sampler and the associated XRF analysis toolchain, a comparison has been made with stationary and personal instruments, namely a SMPS and a DiSCmini using aerosols in the 20-400 nm size range. The number-based data of the two latter instruments were converted to a mass data using a DMA-ELPI setup. This setup provided an estimation of the effective density of the NOAA present in the test aerosols. In all cases, there was a good agreement between the mass calculated from the SMPS data and the mass measured on the filters. The conversion of the DiSCmini data to mass was reliable on the polydisperse TiO₂ aerosol, for which the particle size distribution had optimal properties for the DiSCmini monitor. In the case of classified aerosols (monodisperse aerosols having a geometric standard deviation far from 1.9) the DiSCmini should not be used, as it is recommended by the manufacturer, unless corrections can be performed using the aerosol specific features. The detection limits of the sampler and the associated XRF analysis toolchain were low enough to reliably detect exposure levels below the REL of the NIOSH and INRS for ultrafine ZnO and TiO₂. We have also shown that the NANOBADGE sampler could be used to detect acute exposure events, which are the most frequent case encountered in an industrial setting. The NANOBADGE sampler is thus well suited for epidemiological studies to establish dose-response relationships with respect to NOAA either for short-term exposure (e.g. 15 min time base measurements) or for covering the full shift exposure.

Future work will involve tests of the sampler on real aerosols in the micro-sized range which are representative of NOAA emitted at workplaces [43] and containing background particles and contaminants. It is expected that the ability to quantify the exposure element-wise will provide a high level of details which cannot be accessed using only number-based aerosol instruments.

### 5. Supplementary Material

Stability of the NANOBADGE sampling flowrate, uniformity of aerosol concentrations in the tunnel, particle size distributions of the test aerosols, calibration curves of Zn and Ti for quantitative XRF, sample XRF spectra of filters loaded with TiO₂ and ZnO particles. This material is available online free of charge via the journal webpage.
Acknowledgments

We are grateful to Dr. Ana-Maria Todea, Dr. Christof Asbach, Dr. Martin Fierz and Dr. Michel Pourprix for fruitful discussions on aerosol sampling and data analysis. The present work was performed within the frame of the nanoIndEx project, supported by the French National Funding Agency for Research (ANR), the German Federal Ministry of Education and Research (BMBF), the British Technology Strategy Board (TSB) and the Swiss TEMAS AG, under the frame of SIINN, the ERA-NET for a Safe Implementation of Innovative Nanoscience and Nanotechnology. The research leading to these results has also received funding from the European Union’s FP7 Grant Agreement n. 310584 (NanoReg project).

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