Experimental study of the response functions of direct-reading instruments measuring surface-area concentration of airborne nanostructured particles

Sébastien Bau¹, Olivier Witschger¹, François Gensdarmes² and Dominique Thomas³

¹Institut National de Recherche et de Sécurité, INRS, Laboratoire de Métrologie des Aérosols, Rue du Morvan, CS 60027, 54519 Vandoeuvre Cedex, France.

²Institut de Radioprotection et de Sûreté Nucléaire, IRSN, Laboratoire de Physique et de Métrologie des Aérosols, BP 68, 91192 Gif-sur-Yvette Cedex, France.

³Laboratoire des Sciences du Génie Chimique, LSGC/CNRS, Nancy Université, BP 2041, 54001 Nancy Cedex, France.

E-mail: sebastien.bau@inrs.fr

Abstract. An increasing number of experimental and theoretical studies focus on airborne nanoparticles (NP) in relation with many aspects of risk assessment to move forward our understanding of the hazards, the actual exposures in the workplace, and the limits of engineering controls and personal protective equipment with regard to NP. As a consequence, generating airborne NP with controlled properties constitutes an important challenge. In parallel, toxicological studies have been carried out, and most of them support the concept that surface-area could be a relevant metric for characterizing exposure to airborne NP [1]. To provide NP surface-area concentration measurements, some direct-reading instruments have been designed, based on attachment rate of unipolar ions to NP by diffusion. However, very few information is available concerning the performances of these instruments and the parameters that could affect their responses.

In this context, our work aims at characterizing the actual available instruments providing airborne NP surface-area concentration. The instruments (a- LQ1-DC, Matter Engineering; b- AeroTrak™ 9000, TSI; c- NSAM, TSI model 3550;) are thought to be relevant for further workplace exposure characterization and monitoring. To achieve our work, an experimental facility (named CAIMAN) was specially designed, built and characterized.

1. Materials and methods

1.1. Description of the experimental set-up
A versatile experimental facility, called CAIMAN (for ‘Characterization of Instruments Measuring Aerosols of Nanoparticles’) was designed and built to generate stable and reproducible airborne NP. Within CAIMAN, airborne NP are produced by means of a spark-discharge generator (GFG-1000,
PALAS). The production of airborne NP by spark discharge evaporation has been studied extensively by several authors in different situations [2-12].

This NP generation system allows a variation of both the particle concentration (via the argon and air flow rates, spark-discharge frequency) and their chemical nature by changing the material of the electrodes. In our paper, the results obtained for pure graphite electrodes are presented.

To cover a wide range of electrical charge level and morphology, a bipolar ion generator (EAN 581, TOPAS) and a high-temperature furnace (VECSTAR VTF 7) are included in CAIMAN. Finally, an ageing 2-liter volume is located at the end of the facility from which airborne NP can be sampled. The nanoparticle-free air introduced into the set-up comes from a purification unit (TSI model 3074B), and the excess aerosol is filtered by means of HEPA filters (CAMFIL, model ‘filtre BAG’).

Figure 1 shows a schematic of the CAIMAN experimental facility and lists the properties of the particles that can be varied within each element of the set-up.

In this paper, the CAIMAN facility was only operated on carbon NP; neither the bipolar ions generator nor the high-temperature furnace were used.

1.2. Characterization of the generated airborne NP

The size distribution of the generated airborne NP was measured by a SMPS system (GRIMM SMPS+C, composed of a DMA ‘Vienna Type’ and a CNC model 5.403) operating at a flow rate of
0.3 L/min. This system allows the measurement of the number of particles according to their electrical mobility diameter. Figure 2 presents the count median diameters (CMD) for graphite electrodes as a function of the spark-discharge frequency obtained in our facility operated at constant Argon pressure (1 bar) and two different air pressures (none and 1 bar).

![Figure 2](image)

**Figure 2.** Evolution of the count median diameter of carbon particles produced within the CAIMAN facility (operating conditions: $P_{\text{Ar}} = 1$ bar, $P_{\text{air}} = 0$ and 1 bar)

It can be observed a significant evolution of the CMD as a function of the spark frequency and pressure conditions imposed. An increase of the discharge frequency leads to an increase of the CMD, mainly due to coagulation. This can be partially reduced by adding dilution air, as illustrated in Figure 2 (series corresponding to 1 bar of air), that divides the residence time by a factor of 7. Over all the operating conditions, a wide range of CMD extending from 25 nm to over 150 nm can be obtained. Furthermore, the NP size distributions are quasi lognormal, with geometric standard deviations ($\sigma_g$) ranging from 1.56 to 1.61 in absence of air, and from 1.62 to 1.68 when operating under 1 bar of air. Consequently, due to this slight polydispersion, carbon NP from about 20 to more than 500 nm can be produced within CAIMAN.

In terms of concentrations, real-time measurements were performed to quantify the concentration levels of airborne NP within the facility. Number concentrations in the range $10^4$ to more than $10^7$ #/cm$^3$ and mass concentrations from 0.6 to 6.4 mg/m$^3$ were measured respectively by means of a CNC (Condensation Nucleus Counter GRIMM model 5.403) and TEOM (Tapered Element Oscillating Microbalance, Rupprecht & Patashnick model 1400A).

Furthermore, the airborne NP sampled within the ageing volume were characterized in terms of primary particle size and morphology through the determination of the 2D-fractal dimension. To collect the particles, copper TEM-grids (200 mesh with a carbon film) were taped onto a 25 mm diameter PVC filter (0.08-µm pore size) and air flow was driven from the ageing volume at a flow rate of 1.5 L/min. The primary particle mean size is 16 ± 2 nm, while the 2D-fractal dimension was found to be 1.67 ± 0.03. The fractal dimension was determined by the Box Counting Method [13], which has been previously validated on simulated nanoparticles [14] and here associated to an optimised calculation procedure as proposed by Foroutan-Pour et al. [15].

1.3. Experimental measurement of instruments response functions

The response function, notated $R$, is defined by:

$$R(d_m) = \frac{\text{mean instrument indication}}{\text{mean number concentration}} = \frac{S(d_m)}{N(d_m)} ,$$
where $S$ and $N$ are respectively the NP surface-area and number concentrations.

Experimentally, a parallel measurement of particle number ($N$) and surface-area ($S$) mean concentrations is performed on a monodisperse aerosol of selected mobility size $d_m$ (by using a DMA – Differential Mobility Analyzer GRIMM ‘Vienna Type’) over a stable period of 15 minutes, as shown in Figure 3.

For carbon electrodes, NP with electrical mobility diameters from 20 up to 520 nm have been selected, providing surface-area concentrations significantly over the limit of quantification of the different instruments.

![Figure 3.](image-url)  
*Figure 3. Experimental set-up for the measurement of the response functions of the instruments.*

2. Experimental results

Experimental measurements were performed in monodisperse mode to determine the response functions of the selected instruments as a function of the mobility diameter, as presented in Figure 3.

The results were compared with the existing theoretical responses: lung-deposited surface-areas in alveolar or tracheobronchiolar region for instruments (b) and (c), and active surface-area for instrument (a). The lung-deposited surface-areas were calculated using the lung deposition model developed by ICRP [16] using physiological, worker activity related and aerosol parameters considered by the manufacturer of the NSAM and Aerotrak™ 9000 [17], while active surface-area was obtained with the simplified expression proposed by Jung and Kittelson [18] with $\lambda_{ion} = 15.2$ nm.

Theoretical considerations are then required since raw data have to be corrected. Indeed, even if particles of unique electrical mobility are selected within the DMA, a polydisperse aerosol is obtained at its outlet due to multiple charging of NP with diameters above 50 nm. Consequently, the measured number and surface-area concentrations are due to the contributions of all particles exiting the DMA, i.e. NP of selected mobility carrying $i$ (one and more) electrical charges. The response function experimentally measured is hence defined by:

$$R_{\text{measured}} = \frac{\sum_{i=1}^{n} S_i}{\sum_{i=1}^{n} N_i} \approx \frac{S_1 + S_2}{N_1 + N_2},$$

where indexes 1 and 2 correspond to particles carrying respectively 1 and 2 electrical charges. It should be notified that in this study, particles carrying 3 electrical charges and more are neglected, since they represent a very little fraction of the aerosol.
The fraction of NP at the outlet of the DMA carrying 1 and 2 elementary charges was determined from the DMA transfer function obtained experimentally by Heim et al. [19]. This transfer function is a triangular function taking into account the diffusion of the NP within the DMA. Thus, for a given aerosol entering the DMA, the number and surface-area concentrations of particles carrying 1 and 2 electrical charges can be calculated. Then, the true response functions of the instruments were calculated by correcting the raw data as:

$$R_{\text{corrected}} = \frac{S_1}{N_1} = R_{\text{measured}} \cdot \frac{S_1}{S_1 + S_2} \cdot \frac{N_1}{N_1 + N_2}.$$  

To calculate the number concentrations ratio, the bipolar Fuchs extended model, as described by Wiedensohler [20], was coupled to the DMA transfer function. Notating $f_i(d_m)$ the fraction of particles carrying $i$ elementary charges and $\eta(d_m)$ the DMA transfer function, then the number concentration of particles at the outlet of the DMA carrying $i$ electrical charges is given by:

$$N_i(d_m) = N_0(d_m) \cdot f_i(d_m) \cdot \eta(d_m),$$

where $N_0(d_m)$ correspond to the NP size distribution at the inlet of the DMA. The overall number concentration of particles carrying $i$ electrical charges hence corresponds to:

$$N_i = \sum_{d_m} N_i(d_m).$$

Concerning the fraction of particles carrying $i$ elementary charges, the formalism coming from Wiedensohler [20] and reported in Flagan [21] was used:

$$\log (f_i) = \sum_{j=0}^{j=5} a_j(i) \cdot \left[ \log \left( \frac{d_p}{d_0} \right) \right]^j,$$

where $d_p$ is the particle diameter expressed in nm, $d_0 = 1$ nm is a reference diameter, and $a_j(p)$ are the coefficients of adjustment, reported in Flagan [21]. It should be noted that this relationship is valid for $i = -1, 0, 1$ in the size range 1 to 1000 nm, and for $i = -2, 2$ in the range 20 to 1000 nm.

Then, the ratio in terms of surface-area concentrations can be obtained assuming spherical particles, i.e.:

$$S_i = \sum_{d_m} S_i(d_m) = \sum_{d_m} N_i(d_m) \cdot \pi \cdot d_m^2.$$  

Let us take for example an aerosol with count median diameter $d_{50} = 100$ nm and a geometric standard deviation of $\sigma_g = 1.5$. If the selected size within the DMA is $d_m = 100$ nm, then particles of 156 nm in diameter carrying 2 elementary charges will exit the DMA too. These doubly-charged NP represent 17 % of the aerosol number concentration and 29 % of its surface-area concentration, i.e.:

$$\frac{N_1}{N_1 + N_2} = 0.83,$$

and:

$$\frac{S_1}{S_1 + S_2} = 0.71.$$  

Consequently, the measured response function will be corrected by a factor of 0.86 to take into account the contribution of doubly-charged NP.

To perform this multiple charging correction, the size distribution of the aerosol entering the DMA is required, notated previously $N_0(d_m)$. In our work, the spark-generated NP are not spherical individual particles, but were identified as agglomerates. Lall and Friedlander [22] showed that the electrical mobility diameter of an agglomerate is related to the number and size of the primary
particles it is constituted of. Hence, SMPS-measured particle size distributions \( N_{\text{sph}}(d_m) \) must be corrected by bipolar charging efficiencies of both spheres and agglomerates to obtain the agglomerates size distribution:

\[
N_{\text{agg}}(d_m) = N_{\text{sph}}(d_m) \cdot \frac{\epsilon_{\text{sph}}}{\epsilon_{\text{agg}}},
\]

where \( \epsilon \) correspond to the charging efficiencies. To perform this correction, a primary particle size of 16 nm (see section 1.2.) was used in the calculations of NP concentrations. For example, for the same previous polydisperse aerosol of count median diameter \( d_{50} = 100 \text{ nm} \) and geometric standard deviation of \( \sigma_g = 1.5 \), the ratio of total number concentrations is:

\[
\frac{N_{\text{agg}}(d_m)}{N_{\text{sph}}(d_m)} = 1.02,
\]

value obtained for primary particles of 16 nm.

Both corrections lead to a variation in the response functions (relative difference between raw and corrected data) reaching at maximum 15%.

Figure 4 presents the response functions of the three selected instruments for carbon airborne NP and both configurations (alveolar ‘alv’ or tracheobronchial ‘tb’) for instruments (b) and (c).

Figure 4 shows a good agreement between theoretical curves and corrected experimental responses obtained with carbon airborne NP for particle sizes in the range 20 – 520 nm. Indeed, the biases between experimental data and theory are in the range -45% to +30%.

More precisely, the biases observed for LQ1-DC (Figure 4a) are in the range -40% - +30%, for AeroTrak™ (Figure 4b) between -45% and +30%, and for NSAM (Figure 4c) between -10% and +30%. It should be noted that the three-quarters of the experimental data are in a range of biases to theory of ± 25%.

These new experimental data enrich the actual data base from the works of Shin et al. [23] and Asbach et al. [24] on the NSAM in the range 10 to 400 nm for both ‘alv’ and ‘tb’ configurations. In their studies, NP of sodium chloride (NaCl) were generated by means of an atomizer, and agglomerates of silver (Ag) were produced within a furnace. The NP were then mobility-selected to characterize the instrument.

Concerning the LQ1-DC, the only published data correspond to the size range 20 to 200 nm [25]. In their work, the authors generated silver NP of varying morphology (fractal-like to spherical, 2-D fractal dimensions from 1.58 to 1.94) by means of two furnaces in series.

To our knowledge, our experimental data on the AeroTrak™ 9000 (b) are the first ever published.
To conclude, this experimental study provides new results leading to a better understanding and characterization of three devices devoted to the real-time measurement of airborne NP surface-area concentration. For two of them (NSAM and LQ1-DC), our data enrich and enlarge the size range of the previously published data. Concerning the third instrument, these data constitute the first ever published.

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