Response of three instruments devoted to surface-area for monodisperse and polydisperse aerosols in molecular and transition regimes

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Abstract. An increasing number of experimental and theoretical studies focus on airborne nanoparticles (NP) in relation with many aspects of risk assessment. Indeed, 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 are still under development. Several studies have already identified surface-area as an important determinant of low solubility nanoparticles toxicity. As a consequence, the concept that surface-area could be a relevant metric for characterizing exposure to low solubility airborne NP has been proposed [1]. To provide NP surface-area concentration, some direct-reading instruments have been designed, based on diffusion charging. The actual available instruments providing airborne NP surface-area concentration are studied in this work: LQ1-DC (Matter Engineering), AeroTrak™ 9000 (TSI) and NSAM (TSI model 3550). Their performances regarding monodisperse carbon NP have been investigated by Bau et al. [2]. This work aims at completing the instruments characterization regarding monodisperse NP of other chemical composition (aluminium, copper, silver) and studying their performances against polydisperse aerosols of NP.

1. Introduction
The novel properties of engineered nanostructured particles (NP) and their applications have given birth to technological and economic expectations for industries using NP or products containing NP. However, their unique properties may also make them harmful to humans. Consequently, assessing inhalation exposure to airborne NP constitutes an important challenge.
Several studies have already identified surface area as an important determinant of low solubility nanoparticles toxicity [3-5]. Although there is still considerable uncertainty over how exposure to airborne NP should be most appropriately evaluated, it has been proposed that surface-area measurements should be relevant to a broad range of NP class/attribute combinations [1]. Direct-reading instruments based on diffusion charging have been designed to measure airborne NP active surface-area concentration (LQ1-DC, Matter Engineering) or lung-deposited surface-area concentrations (NSAM model 3550 and AeroTrak™ 9000, TSI Inc.). Their performances regarding monodisperse carbon NP have been investigated by Bau et al. [2].

The aims of this work were (1) to complete previous data on the instrument response functions for monodisperse aerosols with three other chemical substances (aluminum, copper, silver) and (2) to characterize the instruments responses regarding polydisperse aerosols of NP.

2. Materials and methods

2.1. Aerosol production

CAIMAN (for ‘Characterization of Instruments Measuring Aerosols of Nanoparticles’) is a versatile experimental facility that was designed and built to generate stable and reproducible aerosols of nanoparticles (nanoaerosols) with controlled properties (concentration, size, shape, mean charge level). It was initially developed in a collaborative research work within the Aerosol Physics and Metrology Laboratory from the Institut de Radioprotection et de Sûreté Nucléaire (IRSN) and the Aerosol Metrology Laboratory from INRS, which holds the non-transportable facility in its research centre near Nancy, France.

In this facility, airborne NP are produced by means of a spark-discharge generator (GFG-1000, PALAS). In this work, four different electrode materials have been studied: carbon, aluminum, copper and silver. After being generated, further conditioning of the aerosols of NP produced within CAIMAN is achieved by means of:

- a bipolar ion generator (EAN 581, TOPAS) to cover a wide range of electrical mean charge level,
- a high-temperature furnace (CARBOLITE BST16 – maximum operating temperature 1500°C) to provide either partial sintering of agglomerates or coalescence, allowing some degree of control over particle morphology of particles with constant chemistry,
- a 2-liter volume located at the end of the facility from which airborne NP can be sampled and diluted by means of an additional air flow injected at the outlet of the device. It should be noted that this ageing volume is equipped with four sampling lines in parallel, which allows simultaneous measurements.

In this study, neither the ion generator nor the high-temperature furnace were used to modify the properties of the aerosols produced. By varying the operating parameters of the generation, aerosols of NP with differing properties have been produced within CAIMAN. The main characteristics of these aerosols are gathered in Table 1: count median mobility diameter – CMMD – (SMPS), mean agglomerate and primary particle size (TEM-images analysis) and 2D-fractal dimension (TEM-images coupled to an optimized Box Counting procedure described in [2]). The ranges presented in Table 1 were obtained by varying the sparking frequency from 30 to 300 Hz and the air flow introduced into the NP generator from 0 to 20 L/min. All runs were performed with an argon flow rate of 2.5 L/min and a dilution flow rate of 10 L/min introduced into the ageing volume.
Table 1. Characteristic properties of the aerosols of nanoparticles produced within CAIMAN.

| Electrode material | C       | Al      | Cu     | Ag     |
|--------------------|---------|---------|--------|--------|
| Range of CMMD (nm) | 27 – 163| 8 – 50  | 6 – 18 | 6 – 18 |
| Mean size of agglomerates (nm) | 205 ± 95 | 550 ± 46 | 93 ± 26 | 12 ± 3 |
| Primary particle diameter (nm) | 16 ± 2   | 16 ± 3  | 9 ± 2  | N.A.   |
| 2D-fractal dimension (-) | 1.67 ± 0.03 | 1.59 ± 0.02 | 1.55 ± 0.06 | N.A.   |

N.A.: not applicable

Table 1 suggests that the CAIMAN facility provides now well-characterized nanoaerosols at known concentrations, sizes and shapes. In this work, four material electrodes have been used within CAIMAN, presenting count median mobility diameters (CMMD) from 6 to 163 nm. It should be noted that silver electrodes lead to spherical particles; consequently the primary particle size and agglomerate fractal dimensions were not determined for this electrode material.

The output of the CAIMAN facility is very consistent over long time intervals when operating under similar conditions. It indicates that repeatability is one of the important assets of the CAIMAN facility. A more complete description of the features of CAIMAN is available in this issue [6].

2.2. Study of the instruments in monodisperse mode: determination of the response functions

To investigate the response of the instruments in study regarding monodisperse aerosols, a Differential Mobility Analyzer (DMA Grimm Vienna Type, operating flow rate of 0.3 L/min) was placed at the outlet of the ageing volume. Figure 1 is a schematic of the experimental setup.

Figure 1. Experimental setup for the measurement of the response functions of the instruments on monodisperse aerosols at the outlet of CAIMAN.

For a selected particle size $d_m$, the experiments consisted in measuring the lung-deposited (NSAM and Aerotrak™ 9000) and active (LQ1-DC) surface-area concentrations, notated $C_S(d_m,t)$; in parallel, the number concentration was measured by means of a condensation nuclei counter (CNC Grimm model 5.403), notated $C_N(d_m,t)$. 
The instrument response, for the selected size $d_m$, is then related to the mean concentrations measured over 10 minutes:

$$ R(d_m) = \frac{C_S(d_m)}{C_N(d_m)}. $$

It should be mentioned that the majority of particles exiting the DMA carried one negative charge and a small fraction carried two negative charges, they have not been neutralized before measurement with surface area instruments. Particles carrying multiple charges exiting the DMA and measured simultaneously were taken into account according to a classical procedure described in Bau et al. [2].

The slight polydispersion (geometric standard deviations from 1.4 to 1.8) of the aerosols produced allowed the selection and measurement of monodisperse NP depending on their nature: from 20 to 520 nm for carbon, from 15 to 120 nm for aluminum electrodes and from 15 to 100 nm for copper and silver electrodes.

2.3. Study of the instruments in polydisperse mode

The second objective of that study was to investigate the instruments response regarding polydisperse aerosols of NP. This step is particularly interesting because it represents the situations encountered by the instruments in the case of workplace exposure assessment or even environmental monitoring.

The setup used in this configuration is schematized in figure 2.

**Figure 2.** Experimental setup for the measurement of the response functions of the instruments on polydisperse aerosols at the outlet of CAIMAN.

In polydisperse mode, the experiments consisted in measuring in parallel the surface-area concentrations (lung-deposited, active) and the number size distribution of the aerosol (SMPS Grimm composed of Vienna Type DMA and a CNC 5.403). Data from experiments carried out in polydisperse mode were then used to compare surface-area concentrations measured $C_S$ to those calculated ($C_S^*$) from the response function and the number size distribution $C_N(d_m)$ according to:

$$ C_S^* = \sum_{d_m} R(d_m) C_N(d_m). $$
Different operating parameters have been used within CAIMAN to produce aerosols of NP of four substances with count median mobility diameters from 64 to 177 nm (geometric standard deviations from 1.45 to 1.54) and number concentrations between $10^4$ and $15 \times 10^4$ #/cm$^3$. It should be noticed that in this case, the majority of particles carry zero charge as they are used directly from the outlet of the spark discharge generator, as stated in Bau et al. [7].

2.4. Description of the instruments under study

Direct-reading instruments based on diffusion charging have been designed to measure airborne nanostructured particles active surface-area concentration (LQ1-DC, Matter Engineering) or lung-deposited surface-area concentrations (NSAM model 3550 and AeroTrak™ 9000, TSI Inc.). The principle of these instruments is identical: airborne NP entering the device are first electrically charged within a diffusion charger where positive ions attach the particles. An ion trap, positioned at the exit of the charger, removes the ions produced in excess, while the charged particles are collected on a filter. The filter current measured in real-time is then directly correlated to the aerosol flow rate and the number of charges carried by the particles, which is related to their surface-area.

The next subsections briefly describe the instruments examined in this work.

2.4.1. NSAM model 3550 and AeroTrak™ 9000

NSAM and AeroTrak™ 9000 were designed to measure the lung-deposited surface-area concentration of airborne NP either in the alveolar (alv) or in the trachea-bronchiolar (tb) region. This is enabled by adjusting the voltage in the ion trap to manipulate the particle size distribution and therefore the response function (200 V alv, 100 V tb).

Lung-deposited surface-area concentrations correspond to the product of the geometric surface-area and the deposition probability in the considered region:

$$C_{S_{dep,i}} = C_{S_{geo}} \cdot \eta_{dep,i}.$$  

The deposition probabilities $\eta_{dep,i}$ are defined by the lung deposition model developed by ICRP [8] using physiological, worker activity related and aerosol parameters considered by the manufacturer of the NSAM and Aerotrak™ 9000 [9].

2.4.2. LQ1-DC

The LQ1-DC is an instrument designed to measure the active surface-area concentration of airborne NP in real-time.

First introduced by Fuchs [10], the concept of active surface-area represents the fraction of the geometric surface-area of a particle that interacts with surrounding species. In the case of diffusion chargers, the latter correspond to the positive ions produced within the charger and that attach to the surface of the particles. Jung & Kittelson [11] proposed a simplified approach to calculate the active surface-area of a spherical particle according to:

$$S_{act} = S_{geo} \cdot \frac{Cu^* \alpha \lambda_{ion}^{Cu^*}}{Cu \lambda_{ion}^{Cu}}.$$  

where:

$$Cu^* \lambda_{ion}^{Cu^*} \approx 2 \lambda_{ion}^{Cu^*} \frac{d_p}{d_p} + \beta \gamma$$ and $Cu \lambda_{ion}^{Cu} \approx 2 \lambda_{ion}^{Cu} \frac{d_p}{d_p} \left[ \alpha + \beta \exp \left( \frac{d_p \cdot \gamma}{2 - \lambda_{ion}} \right) \right].$

In these equations, $\alpha$, $\beta$ and $\gamma$ are the slip correction coefficients, taken for 1.165, 0.483 and 0.997 respectively according to Kim et al. [12]. The ion mean free path $\lambda_{ion}$ was 15.2 nm.
3. Experimental results

3.1. Monodisperse mode
The response functions measured with monodisperse aerosols were found in good agreement with theoretical curves in the range from 15 to 520 nm for the three devices in the case for carbon [2]. The same behavior was observed for the three other substances (copper, aluminum, silver); the biases between experimental data and theory are in the range -45 % to +50 %.

More precisely, the biases observed for LQ1-DC are in the range -40 % to +30 %, for AeroTrak™ 9000 between -45 % and +30 %, and for NSAM 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 %.

3.2. Polydisperse mode
As stated in paragraph 2.3, the surface-area concentrations were measured and calculated from the SMPS number size distribution coupled to the experimental response functions measured for monodisperse NP. Figure 3 presents the comparison between measured and calculated surface-area concentrations (active and lung-deposited) for all conditions.

Whatever the instrument considered, it can be observed from figure 3 that there are deviations between measured and calculated surface-area concentrations. Over all experiments, the relative discrepancies are found between -35% and +150%. They are calculated by:

$$\Delta(\%) = \frac{C^*_S - C_S}{C_S} \times 100 \%.$$  

Table 2 presents the range of biases for each instrument in study.

| Instrument                  | Range of bias |
|-----------------------------|---------------|
| NSAM – alv. deposition      | -11% - +103%  |
| AeroTrak™ 9000 – alv. deposition | -6% - +43% |
| NSAM – tb. deposition       | 0% - +107%    |
| AeroTrak™ 9000 – tb. deposition | +11% - +150% |
| LQ1-DC                      | -35% - +117%  |

The discrepancies observed are quite important, which led us to formulate hypothesis to explain these deviations.
Figure 3. Experimental results for polydisperse aerosols.
3.2.1. Influence of airborne NP number concentration

The first parameter that might influence the response of the instruments is the total concentration of the aerosol. Indeed, the charging efficiency of the diffusion chargers can be varied, leading to different number of elementary charges carried by the particles. To examine this effect, two conditions (named “A” and “B”) with identical relative number size distribution have been compared. Table 3 presents the main characteristics of these polydisperse aerosols.

| Configuration | A               | B               |
|---------------|-----------------|-----------------|
| CMMD (nm)     | 64.5            | 65.7            |
| GSD (-)       | 1.53            | 1.53            |
| Total number concentration (#/cm$^3$) | $1.493 \times 10^5$ | $4.905 \times 10^4$ |
| Electrode material | Ag              | Ag              |

For these configurations, the ratio ($r$) of the number concentrations per channel is constant over the whole range of particle size:

$$r \equiv \frac{C_N \cdot C_m \cdot A}{C_N \cdot C_m \cdot B} = 3.03 \pm 0.15 \approx K.$$  

As a consequence, the ratio of the surface-area concentrations should be found near the value of 3. However, our results indicate that the experimental ratios range from 3.33 for NSAM in “alv” configuration to 1.89 for AeroTrak™ 9000 in “tb” configuration. LQ1-DC is placed in between with a ratio of 2.13. This indicates that measured surface-area concentration is not proportional to the number concentration of the particles, whatever the instrument used.

This observation then led us to investigate the influence of the charge distribution of the particles on the signal measured by the diffusion chargers.

3.2.2. Influence of airborne NP electrical charge distribution

Within a diffusion charger, particles carry $p$ elementary charges, depending on (1) the ion concentration $N_i$, (2) their residence time within the charger $t$, and (3) their size $d_p$. The current $I$ measured on the filter of the instruments corresponds to the total amount of electrical charges deposited, i.e.:

$$I = e \cdot Q \cdot \sum_{d_p} p \cdot C_N \cdot C_m \cdot l_p \cdot C_d.$$  

From this current, surface-area concentration is obtained by means of a linear relationship established by the manufacturer:

$$C_S = \alpha \cdot I,$$

where $\alpha$ is a constant determined after calibration. Physically, this parameter is a complex function depending mainly on attachment coefficients of ions to particles surface, $N_i \cdot t$ product of the charger, number concentration, shape, and size of the particles.

Because particles of size $d_p$ do not all carry the same number of elementary charges, there are configurations where the total amount of electrical charges is the same while the surface-area is different. The numeric values taken as a reference were published by Biskos et al. [13] and were obtained with a unipolar diffusion charger with $N_i \cdot t = 1.97 \times 10^{15}$ ions.s/m$^3$.

For example, a concentration of 10 #/cm$^3$ of 40-nm particles will lead to the measurement of the same current than a concentration of 4 #/cm$^3$ of 120-nm particles. According to the last equation, the instrument will indicate the same surface-area concentration. However, the 120-nm particles, even less in terms of number concentration, represent 3.6 times more in terms of geometric surface-area. This effect can result in differences in the measurement of polydisperse aerosols; nevertheless it is difficult to conclude whether this effect will over or underestimate the true surface-area concentration.
4. Conclusion
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. It should be reminded that this parameter has been highlighted by several toxicological studies for the case of insoluble NP but is not associated to standardized measurement method yet.

The first part of this work was devoted to the measurement of the response function of the instruments regarding monodisperse NP. For the instruments NSAM and LQ1-DC, our experimental data enrich and enlarge the size range of the previously published data [14-16]. Concerning the third instrument AeroTrak™ 9000, these data constitute the first ever published.

In a second step, instruments were used to measure the surface-area concentration of polydisperse airborne NP. Calculations from SMPS size distributions and response functions for monodisperse NP were compared to responses of the instruments obtained for polydisperse NP, showing discrepancies from -36% to +150%. Hypotheses were formulated to interpret the deviations observed; in particular, the influence of the total number concentration of NP and their electrical charge distribution were identified as sources of bias.

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