CAIMAN: a versatile facility to produce aerosols of nanoparticles

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Abstract. This work aims at presenting a nanoparticle generation non-transportable facility in aerosol phase called “CAIMAN” (acronym for Characterization of Instruments Measuring Aerosols of Nanoparticles) and its performances. This facility delivers primary nano-aerosols from electrodes made of C, Al, Cu (and mixtures containing Be), Ag, Constantane (a mixture of Cu-55wt% and Ni-45wt%) particles at known concentrations, sizes, shapes and mean charge levels. It is also capable to deliver well-known particle mixture containing combinations of the “primary” nano-aerosols and particles representative of background aerosols (in the present work NaCl). The output of the CAIMAN facility is very consistent over long time intervals when operating under similar conditions. It indicates that repeatability is also one of the important assets of the facility.

1. Introduction
Rationally designed, manufactured nano-objects (nanoparticles and nanostructured particles – NP) attract a great deal of interest, due to their many technologically interesting properties. The properties of NP and their applications have given birth to technological and economic expectations for industries using NP or materials/end products containing NP (nanomaterials). However, some of these properties have given rise to concern that they may be harmful to humans.

In the workplaces where NP are manufactured or used, exposure to airborne NP is plausible at all phases of the nanomaterial life cycle, although the nature, level of exposure and the number of person involved could differ greatly. One major uncertainty in the health risk assessment of NP arises from the lack of knowledge of their physicochemical properties and behavior in the airborne state (aerosol phase).

Among the technical challenges ahead for assessing workers exposures to NP are to:

- redesign and evaluate “NP-capable” instruments already in laboratory use into portable and affordable devices, and
- expand the sensing technology available for NP detection by adopting new options with realistic potential for real-time measurement and compact design.

To investigate the performances of these instruments and technologies, the aim of this work was to design an experimental facility able to produce aerosols of NP with controlled properties in various situations. This paper describes the CAIMAN setup and its main characteristics.
2. Description of the experimental setup (CAIMAN)
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.
Figure 1 shows a schematic of the CAIMAN experimental facility in its standard configuration. A different arrangement has been used for producing mixture of NP and particles representing background aerosols (see paragraph 3.7).

Within CAIMAN, the particle-free air introduced into different points of 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’).

Following sections briefly describe each of the elements constituting the CAIMAN facility, i.e. an airborne NP generator, a bipolar ion generator, a high-temperature furnace and a home-made ageing volume.

2.1. Airborne NP generation
Within CAIMAN, airborne NP are produced by means of a spark-discharge generator (GFG-1000, PALAS). The production of airborne NP by spark discharge has been studied extensively by several authors in different situations [1-15].

Aerosol production rate varies by adjusting the spark-discharge frequency $\omega$, which is directly controlled by the potentiometer setting of the GFG-1000 PALAS, and the flow rates of argon shielding and primary dilution by air. Consequently, 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. Presently, seven different electrode materials have been studied, which chemical composition was determined by ICP-MS and gathered in table 1.

| Electrode                  | Composition                                                                 |
|----------------------------|-----------------------------------------------------------------------------|
| Carbon                     | Graphite (pure)                                                             |
| Aluminum (type 2071A)      | Al(93.1%) – Cu(4.8%) – Fe(0.7%) – Mn(0.6%) – Si(0.5%) – Mg(0.3%)            |
| Copper                     | Cu(99.45%) - Al(0.5%) – Si(0.04%)                                          |
| Silver                     | Ag > 99.99%                                                                 |
| Constantane                | Cu(55%) – Ni(45%)                                                           |
| Cu/Be^2                    | Cu(98%) – Be(1.9%) – Co(0.2%) – Pb(0.3%)                                    |
| Cu/Co/Be^2                 | Cu(95.6%) – Be(0.5%) – Co(2.4%)                                            |

^1 Delivered by Palas
^2 Delivered by Goodfellow

2.2. Airborne NP state-of-charge
To cover a wide range of electrical mean charge level, a bipolar ion generator (EAN 581, TOPAS) is included in CAIMAN at the outlet of the NP generator. Its principle is based on air ionisation by corona charging in two independent chambers. Positive and negative ions can be produced separately in each chamber, and then mixed consecutively with the particles within a mixing chamber which geometry was optimised to increase particle charging efficiency. Both the air flow rate and the corona charger parameters (voltage and current) can be adjusted, allowing a wide range of NP electrical state-of-charge. Further elements can be found in the work of Marquard et al. [16, 17] in unipolar mode.

2.3. Airborne NP morphology
Morphology being another key-parameter of the NP produced within CAIMAN, a high-temperature furnace (CARBOLITE BST16 – maximum operating temperature 1500°C) was inserted in the facility. Indeed, several studies [18-28] have shown particle restructuration by sintering under high temperatures. The high-temperature furnace can be operated at different temperatures to provide either partial sintering of agglomerates or coalescence, allowing some degree of control over particle morphology of particles with constant chemistry.

2.4. Airborne NP sampling and measurement
The aerosol leaving the furnace is allowed to age in a 2-liter volume located at the end of the facility (see figure 1) 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. Obviously, more instruments can be connected if flow splitters are put into line. For testing with monodisperse particles, a DMA can be connected at one of the four outputs. Connections are in metric but any other connections can easily be used.

It should be noted that CAIMAN can only be used with aspirating aerosol instruments.

2.5. Safety issues
Due to strong nuclear safety regulation in France, no radioactive source can be brought to the Institute. The only radioactive source hold by the Aerosol Metrology Laboratory is an Am^{241} sealed source devoted to the Grimm DMA.

The entire CAIMAN facility is confined as shown in figure 2.

The first part of the facility is contained within a box containment system (4m x 0.8m x 0.8m) that limits any worker exposure from accidental release from the generator to the entrance of the ageing chamber. The second part of the facility is located within a constant velocity 2-m large fume hood.
3. Features of CAIMAN

In this section, key properties of the aerosols of NP produced within CAIMAN are exposed. For all experiments, argon flow $Q_1$ was fixed to 2.5 L/min and ageing volume flow to $Q_5 = 10$ L/min; configuration 1 refers to air flow $Q_2 = 0$ while configuration 2 refers to $Q_2 = 20$ L/min. According to PALAS, the frequency indication ($\omega$) is related to spark discharge frequency $f$ by $f = 0.3 \omega$.

3.1. Generation stability

Before comprehensive characterization of the airborne NP produced within CAIMAN, the generation stability was tested over 170 minutes for carbon electrodes in configuration 2 and $\omega = 1000$ a.u. The 46 scans measured by the SMPS showed a variation of $\pm 4\%$ in terms of count median mobility diameter (CMMD) relative to its mean value over all scans as calculated by:

$$\text{ratio} = \frac{\text{CMMD (scan i)}}{\text{CMMD (all scans)}}$$

Figure 3 shows the results obtained.

![Figure 3. CMMD for Carbon electrodes in configuration 2 and $\omega = 300$ a.u. over 170 min](image)

The mass concentration of the aerosol produced was also monitored by means of a TEOM microbalance, leading to a variability of $\pm 7\%$ during a measurement period of 1 hour, as shown in figure 4.
In terms of total number concentration of airborne NP, variations below 4% were observed over 4 hours of generation. Furthermore, reproducibility of the generation was tested (same operating parameters set with one week delay) and showed a close agreement between NP size distributions (less than 10% variation in terms of total concentration and CMMD).

3.2. Number size distributions
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 (from 5.5 to 350 nm with the middle size DMA, and from 11 to 1080 nm with the long DMA). The choice of the DMA was adapted depending on the median size of the aerosols measured to provide most of the distribution.

Figure 5 presents the count median mobility diameters (CMMD) for all types of electrode as a function of the spark-discharge frequency for configurations 1 and 2 respectively.

**Figure 5.** Airborne NP count median mobility diameter for the different materials (derived from SMPS data)
It can be observed a significant evolution of the CMMD as a function of the spark frequency and additional air flow conditions imposed. In configuration 1, CMMD were found between 17 nm and 228 nm. In configuration 2, the range of CMMD extends from 7 to 87 nm. This decrease in particle size can be linked to lower coagulation effects by (1) dilution due to additional 20 L/min air flow rate, and (2) decrease of residence time (by a factor of 9).

From TEM micrographs, it can be seen that all collected NP are aggregates, except those stemming from Silver which are spherical. This might be due to the non oxidation of Silver-based NP, which enables primary particles to coalesce in absence of an oxidation layer, leading to metal-metal contacts, as stated by Tabrizi et al. [11].

3.3. Mass concentrations

A previous study carried out on another CAIMAN configuration allowed this determination by means of a TEOM system. If the data cannot be directly used because of configuration modification of CAIMAN, table 2 presents the range of mass concentrations of airborne NP produced and maximum mass production rate.

| Electrode | Range of mass concentration (µg/m³) | Maximum mass rate (µg/h) |
|-----------|-------------------------------------|-------------------------|
| C         | 800 – 6400                          | 4800                    |
| Al        | < 20 – 450                           | 340                     |
| Cu        | < 20 – 240                           | 180                     |
| Ag        | < 20 - 680                           | 510                     |
| Cu/Be     | 110 – 1800                           | 1350                    |
| Cu/Co/Be  | 140 – 740                            | 555                     |

3.4. Electrical state-of-charge

The mean charge per airborne NP generated within our facility was determined by the simultaneous measurement of the number concentration (GRIMM CNC model 5.403) and current (electrometer TSI model 3068B). The mean charge per particle (\( \bar{p} \)) is given by:

\[
\bar{p} = \frac{I}{C_N \cdot e \cdot Q}
\]

where \( C_N \) corresponds to the mean number concentration of airborne NP (measured by the CNC), I is the mean current (measured by the electrometer), \( e \) represents the elementary charge (\( e = 1.6 \cdot 10^{-19} \) C) and Q is the flow rate of the electrometer (adjusted from 0.3 to 5 L/min to measure a current well above the limit of quantification of the electrometer).

The same behavior can be noted for each electrode material. For sparking frequencies below 200-300 a.u., the raw mean charge per particle is negative, and becomes positive for sparking frequencies above this limit. The addition of ions produced within the ion generator lead to a wide range of possibilities in terms of electrical state-of-charge of airborne NP, summarized in table 3.
Table 3. Range of variation of the mean charge per particle of airborne NP

| Electrode material | Range of variation of | Configuration |
|--------------------|-----------------------|---------------|
|                    | raw $-\bar{q}$ | $\bar{q}$ with $\Theta$ ions | $\bar{q}$ with $\Theta$ ions | |
| C                  | -1.61 | 0.94 | 1.11 | 3.09 | -1.59 | -2.46 | 1 |
|                    | -0.25 | 0.18 | 0.40 | 0.58 | -0.33 | -0.88 | 2 |
| Al                 | -0.53 | 0.48 | 0.43 | 1.11 | -0.32 | -1.60 | 1 |
|                    | -0.11 | 0.05 | 0.09 | 0.21 | -0.13 | -0.24 | 2 |
| Cu                 | -0.08 | 0.05 | 0.07 | 0.39 | -0.19 | -0.46 | 1 |
|                    | 0.00  | 0.01 | 0.06 | 0.13 | -0.08 | -0.21 | 2 |
| Ag                 | -0.02 | 0.02 | 0.19 | 0.33 | -0.16 | -0.49 | 1 |
|                    | -0.01 | 0.01 | 0.03 | 0.05 | -0.04 | -0.07 | 2 |
| Constantane        | -0.44 | 0.31 | 0.89 | 2.04 | -0.78 | -1.99 | 1 |
|                    | -0.03 | 0.04 | 0.13 | 0.26 | -0.13 | -0.29 | 2 |

3.5. Particle shape

Partial sintering of primary particles constituting aggregates of Aluminum-based NP was observed by use of the high-temperature furnace. As a consequence, airborne NP morphology was varied from chain-like aggregates to “compact” aggregates when increasing the temperature within the furnace. In parallel of NP sampling, SMPS number size distributions were measured, as presented in figure 6.

Figure 6. Effect of the furnace temperature on the number size distributions measured for Aluminum electrodes in configuration 1, $\omega = 1000$ a.u.

Figure 7 presents TEM pictures of sampled Aluminum-based NP for the different temperatures. Particle restructuring can be highlighted in these pictures when increasing temperature.

From figure 7, it can be observed that particles tend to be more compact when temperature increases. This feature may be useful for studying the effect of particle morphology with constant chemistry on instruments behavior.
Figure 7. Change of morphologies for airborne NP for Aluminum electrodes at various sintering temperatures: ambient temperature (20°C), sintering at 900°C; sintering at 1200°C; sintering at 1500°C.

3.6. Aerosol dilution
To avoid saturating the instruments in study, airborne NP were produced from Carbon electrodes with $\omega = 1000$ a.u. The additional air flow rate injected within the ageing volume (notated $Q_5$) was successively set to 10 (normal configuration), 20, 30, 40 and 50 L/min. Table 4 presents, for both configurations, the evolution of aerosol CMMD and the number concentrations ratio calculated by:

$$\text{ratio} = \frac{C_N Q_5}{C_N Q_5 = 10 \text{ L/min}}.$$

Table 4. Effect of the dilution flow rate ($Q_5$) on the relative number size distributions measured for Carbon electrodes with $\omega = 1000$ a.u. and varying additional air flow rates $Q_5$

| $Q_5$ (L/min) | Configuration 1 | Configuration 2 |
|--------------|-----------------|-----------------|
|              | CMMD (nm)       | Ratio | CMMD (nm) | Ratio |
| 10           | 248             | -     | 93         | -     |
| 20           | 234             | 0.69  | 90         | 0.88  |
| 30           | 233             | 0.50  | 86         | 0.69  |
| 40           | 232             | 0.39  | 83         | 0.58  |
| 50           | 231             | 0.32  | 81         | 0.51  |
It can be observed from this table that the aerosol characteristics are almost independent from the additional air flow, dilution factors up to 3.1 can be obtained without significant change of the airborne NP number size distribution.

3.7. Particle mixture (NP together with background aerosols)
One requirement of test facilities is the possibility to deliver well-known particle mixture containing combinations of the “primary” nanoaerosols together with particles representatives of background aerosols. The initial CAIMAN configuration has been redesigned to produce not only the “primary” nanoaerosol (standard configuration) but also a known particle mixture containing combinations of the “primary” nanoaerosol and particles representatives of background aerosols. In the present work, preliminary tests have been carried out with NaCl particles as being representatives of background aerosols. The Laskin-type nebulizer was chosen as generation system. The aerosol of NP produced within CAIMAN was mixed to an aerosol of NaCl crystals at the inlet of the ageing volume. The preliminary experiments were performed with an aqueous solution of NaCl at a concentration of 0.5 g/L and an air flow rate of 20 L/min within the Laskin-type nebulizer. SMPS measurements are shown in figure 9, where the finer mode (23 nm) corresponds to the NaCl particles and the larger one (350 nm) to the carbon particles.

![Figure 8](image-url)

**Figure 8.** Number size distribution of the particle mixture obtained from Carbon electrodes and NaCl particles. The finer mode (23 nm) corresponds to NaCl particles and the larger one (350 nm) to C particles.

4. Conclusion
In this work, the performances of the CAIMAN non-transportable facility have been evaluated. The CAIMAN facility provides now well-characterized “primary” nanoaerosols at known concentrations, sizes, shapes and mean charge levels. Within CAIMAN, nanoaerosols are produced by means of a spark-discharge generator (GFG-1000, PALAS). Until now, seven material electrodes have been used within CAIMAN: Carbon (delivered by PALAS), Aluminum (type 2071A), Copper, Silver, Constantane, Cu/Be and Cu/Co/Be.

The airborne NP characterized in this work present count median mobility diameters from 7 to 228 nm, with number concentrations varying from $1.7 \times 10^6$ to $1.8 \times 10^7$ #/cm$^3$.
The standard configuration of CAIMAN has been redesigned to produce not only the “primary” nanoaerosol but also a known particle mixture containing combinations of the “primary” nanoaerosol and particles representatives of background aerosol. In the present work, tests have been made with NaCl. The output of the CAIMAN facility is now 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.

Acknowledgments
The research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement n°211464-2.
Authors would like to thank S. Veissiere from INRS for the TEM pictures.

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