Specific response of SMPS particle counter to CNT

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Abstract. The aim of this work is to evaluate the ability of conventional particle detection like SMPS tools calibrated for spherical particles to measure CNTs which present both a nanometre and a micrometre size. Using such conventional measurement tools for the detection of CNTs would be of particular interest. The SMPS gives numbers in terms of concentration and electrical mobility diameter. A theoretical approach is first explored in order to predict the spherical equivalent diameter for CNTs as seen by a SMPS. Experimental measurements were performed in order to validate the theoretical estimations.

1. Introduction
The difficulty in characterizing CNTs from a SMPS (Scanning Mobility Particle Sizer) response is that both the diameter and the CNT length must be determined. SMPS is composed of two parts: the Differential Mobility Analyzer (DMA) + and the Condensation Particle Counter (CPC). DMA classifies particles and CPC counts the particles with a given size. The SMPS response is in direct relation with the CNTs (Carbon Nanotubes) transport thought the DMA. The latter is influenced by CNTs peculiar shape. Only few studies have been carried out about the effect of asphericity on the equivalent spherical mobility diameter. Some theories are developed for the transport of aggregates or aspherical particles in the DMA [1]. Zelenyk et al. [1] demonstrates that in intense electric fields, high aspect ratio particles tend to orient parallel to the electric field. At lower electric fields, particles are in random orientation [1]. Some approaches of the response of SMPS to carbon nanotubes have been also identified. CNTs of length 52 nm and diameter 6.5 nm were measured during the process at an equivalent sphere diameter of 23 nm [2]. Unrau et al. [3] produced Single Wall CNTs in diffusion flames and used a SMPS for online measurements of the synthesized particles. They were able to evaluate the effectiveness of the synthesis by observing a bimodal size distribution corresponding to catalyst particles and nanotubes. SWCNT of diameter 2 nm and length 1 µm were observed at an equivalent sphere diameter of 48 nm. Some studies about measurement of aspherical particles by SMPS show that this relation is confirmed experimentally for particles with small length and diameter [4, 5]. Kim et al. [6] calculated the behaviour of singly charged cylinders undergoing Brownian motion in an electric field considering their polarization to explain their travelling trough the DMA. Cylinders with small aspects ratios tend to rotate freely; they are undergoing the Brownian motion. When the aspect
ratio increases and over a critical value of $\beta$, the cylinders tend to align with the electric field, $\beta$ is the ratio of the cylinder length to the cylinder diameter.

The aim of this work is to evaluate the ability of conventional particle detection like SMPS tools calibrated for spherical particles to measure CNTs which present both a nanometre and a micrometre size. A theoretical approach is explored in order to predict the spherical equivalent diameter given by the SMPS for CNTs with different aspect ratio. Experimental measurements are performed in order to validate the theoretical approach. The detection limits of the SMPS to CNTs are also given. The detection limits of the apparatus in terms of CNTs dimensions are specific to the material used for SMPS (geometry, air flow rate).

2. Theoretical approach
A simplified version of calculations given by Kim et al. [6] is proposed in this paper. Prediction of the CNTs length can be carried out by two explicit expressions of the relationship between the nanotube length and the sphere equivalent diameter. Cylinders with $\beta < \beta_1$ and high aspect ratios have a random orientation when travelling through the DMA. $\beta$ is the ratio of the cylinder length to the cylinder diameter. The effective length of the particle can be calculated by:

$$ L = \frac{6Kd_{sph}}{d_{cyl} C(d_{sph})} $$

with $d_{sph}$ the sphere equivalent diameter measured by the SMPS, $d_{cyl}$ the diameter of the cylindrical particle and $C(d_{sph})$ the Cunningham slip correction in air equal to:

$$ C(d_{sph}) = 1 + 2.492 \frac{a}{d_{sph}} + 0.84 \exp(-0.43d_{sph}/a) $$

with $a$ the mean free path (dependant on the temperature and pressure) and $K \sim 0.512$.

Cylinders with $\beta > \beta_2$ and high aspect ratios are aligned with the electric field.

$$ L = \frac{6ad_{sph}}{0.9d_{cyl} C(d_{sph})} $$

![Figure 1. Estimation of equivalent sphere diameter for several nanotube lengths and diameters.](image)

The estimation of the equivalent spherical diameter $d_{sph}$ was performed for several nanotube lengths and diameters (Figure 1). The curves are plotted for aerosol in air, for a maximum $d_{sph}$ of 1 µm corresponding to the ‘long’ DMA. In black is represented the limit of prolate nanotubes ($L = d$). In light respectively dark gray are represented the detection limits of the SMPS ($d_{sph} = 10$ nm and 1 µm). The transition from random orientation to aligned particles ($\beta_1 < \beta$ and $\beta < \beta_2$) depends on the geometry.
of the SMPS used. For high sphere equivalent diameters (dark gray curves 200 nm – 1 µm) nanotubes are aligned with the electric field. For small sphere equivalent diameters (light gray curves 10 - 60 nm) nanotubes are randomly oriented.

3. Experimental procedure

3.1. Aerosol generation from a liquid dispersion
SMPS measurements were carried out on CNTs dispersed in air. Nanotubes were generated from CNTs dispersion in solutions and generated by atomisation. They present a diameter of 1.4 nm and a length of several microns. An atomizer model TSI 3076 is used to generate a spray of droplets containing CNTs. The aerosol was dried in a high flow rate of compressed air before entering the measuring tools. First, stable dispersions were obtained using surfactant (as shown in Figure 2). A surfactant was used to enhance electrostatic repulsion leading to a better dispersion stability. Two surfactants were tested: CTAB and Triton X-100. An ultrasonic probe of 200 W was used to disperse and break the CNTs.

3.2 Aerosol generation from CNTs deposited on a wafer – Dry way
The CNT aerosol was also generated by a dry process. The CNTs were grown by PECVD on a Si wafer as shown on the picture taken by SEM (Figure 3). They have a “bamboo-like structure”. The fabrication process allows to vary the CNTs diameter and length. The dimensions of the CNTs are given in Table 1.
In order to generate the aerosol, a rotating brush placed on a tool and turning at a speed of 10 000 tr/min was used to smoothly scratch the wafer in a glove box (Figure 4). The experiment was carried out in a glove box in order to get a low background level of nanoparticles: a HEPA filter maintained a clean air in the box.

The SMPS aspiration was directly positioned over the wafer to collect most of the released CNTs.

### 3.3 Description of the detection instrument

The SMPS determines the particles size distribution according to their electrical mobility. The DMA is composed of a cylinder with a negatively charged rod at the centre. The particles move in a laminar flow toward the central rod if positively charged at a rate determined by their electrical mobility. The output flow contains a monodispersed aerosol which goes in a CPC. A DMA (model 5.5-900, Grimm) and a Condensation Particle Counter (CPC model 5.403, Grimm) is used. The concentration at one size is determined by counting the particle after their artificial grow in a buthanol cloud. A $^{85}$Kr radioactive source is used in order to neutralize the nanoaerosol before introducing into the DMA. A long DMA measures particles between 10 nm and 1 µm. The characteristics are listed here after: sheath air flow = 3 L/min, dimensions of the electrode: length = 35 cm, internal diameter 10 mm, external diameter 20 mm.

### 4. Results and discussion

#### 4.1. Detection of CNTs aerosolized from stable dispersions

Stable dispersions containing NTC were aerosolized in the air. First measurements of CTAB solutions with and without CNTs were carried out with the SMPS (Figure 5). No significant differences can be noted between the 2 curves. The surfactant seems to create an important parasitic signal: we can hardly draw conclusion about the detection zone of the CNTs. Results shows that the use of surfactant to stabilize the dispersion, can induce a very large amount of background noise, masking the CNT contribution. We did not reach to eliminate this background level even with low surfactant concentration. This is why a dry procedure was tested as well.

### Table 1. Characteristics of the tested CNTs.

| Sample | Length (µm) | Diameter(nm) |
|--------|-------------|--------------|
| 1      | 0.3         | 90           |
| 2      | 0.9         | 90           |
| 3      | 1.2         | 100          |

![Figure 4. Schematic of the dry way aerolisation method.](image-url)
4.2. Detection of CNTs aerosolized in air

Tests were performed on CNTs with different aspect ratio in order to validate the theoretical approach. First measurements were carried out on Sample 1, Sample 2, Sample 3 (Table 1). The background, including the rotation of the brush on the wafer, is less than 20 part/cc which is negligible. An example is given in the Figure 6: CNTs were detected with an equivalent sphere diameter centred around 200 nm. A second peak is also centred around 100 nm as shown on the second measure. This is supposed to be due to CNTs broken during the scratching or to the bad growth of some CNTs on the wafer.

Figure 7 shows the estimation of the spherical equivalent diameter for the SMPS for CNTs. The detection zones for the aerosolized CNTs are represented also on the Figure 7. In order to define the detection zones: the width at half weight for the Gaussian peak detected by the SMPS was taken. The length variation induced by the fabrication process, is estimated from the SEM image taken on the wafer. The first parts of the curves are dotted because they do not agree with the assumption of high aspect ratio. The transition from the regime ”random orientation” to ”aligned particles” has been estimated. Experimental results fit quite well with the theoretical approach. Generally speaking, the measured equivalent sphere diameters were situated between the ‘randomly oriented’ curve and the ‘aligned’ curve. For CNTs (L = 300 nm, d = 90 nm), the prediction slightly underestimates the equivalent sphere diameter. This deviation may be due to the uncertainty of the transition zone from the ‘randomly oriented’ curve and the ‘aligned’ curve used. For longer CNTs (L = 900 nm, d = 90 nm, L = 1200 nm, d = 100 nm), the prediction is slightly overestimating the equivalent sphere diameter.
According to Kim et al., this may be caused by the bent structure of the CNT which modifies the drag force.

![Figure 7. Estimation of the equivalent spherical diameter for Grimm SMPS and experimental results.](image)

**5. Conclusions**

Detection of aerosolized CNTs from dispersed liquid appears masked by the surfactant. CNTs generation by a dry way allows to detect CNTs by the SMPS. The SMPS is able to detect, count and measure CNTs, however the equivalent sphere diameter response of the apparatus must be considered very carefully. Considering unitary and straight CNTs, a calculation of equivalent-spherical diameter (NTC length and diameter) is proposed for a standard SMPS (10 nm -1 µm). First experimental results fit quite well with this theoretical approach.

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