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# A TEM-based method as an alternative to the BET method for measuring off-line the specific surface area of nanoaerosols

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ABSTRACT

At the present time, no stabilised method exists allowing an estimation of the specific surface area for airborne nanostructured particles (nanoaerosols). Recent toxicological studies have, however, revealed biological effects linked to the surface area of these particles. Only the BET method, which can determine the specific mass surface area of a powder, constitutes a reference both in toxicology and in the materials domain. However, this technique is not applicable to nanostructured aerosols given the mass quantities of particles required (between approximately some mg to hundreds of mg taking into account the limit of quantification of existing BET instruments).

To characterise the specific surface area of airborne nanostructured particles, a method based on analysing transmission electron microscopy (TEM) images is proposed. This has recourse in particular to previous work carried out in the area of nanoparticles originating from combustion (soot), and takes into account structural parameters of nanostructured particles including the number distribution of primary particles, their overlap coefficient and the fractal dimension of agglomerates and aggregates.

The approach proposed in this work was applied to five commercially-available nanostructured powders of differing natures ($SiO_2$, $ZrO_2$, $Al_2O_3$, $Fe_2O_3$ and $Fe_3O_4$). This first involved their prior analysis by the BET method and then being placed in suspension in aerosol form using a vortex-type shaker system. The procedure to calculate the specific surface area using image analysis was then applied to the sampled aerosols and compared to the BET measurements. The experimental results obtained on the five nanostructured powders cover a range of specific surface areas from 20 to 200 $m^2/g$, the primary particles having mean diameters varying from 7 to 47 nm. Close agreement was observed between the two approaches which, taking into account measurement uncertainties, are statistically equivalent at significance level $\alpha = 0.05$.



## 1. Introduction

Nanomaterials are defined as materials having constitutive elements with external dimension in the nanoscale (i.e. between approximately 1 and 100 nm), and which are designed with specific properties in mind [1–3]. Indeed, the physical, chemical and/or biological properties of traditional materials can evolve as a function of the size of the constitutive elements until they become very different from those that can be observed for the solid material [4].

Hansen et al. [5] established a classification of nanomaterials. Their work has resulted in a division of nanomaterials into three categories: (1) volume nanostructured materials such as nanoporous materials, the ceramic zeolites used in the field of catalysis, etc., (2) surface nanostructured materials including surface coatings applied to glass with self-cleaning properties, etc., and (3) materials made up of nanostructured particles, for example colloidal suspensions, nanostructured powders, nanocomposites and nanostructured aerosols.

In addition, the specific properties of nanomaterials are partly linked to their high surface area to volume ratio. Thus, the specific surface area constitutes a dominant characteristic of nanostructured particles.

Nanostructured particles, which can come from nanomaterials in divided form, have also been classified in the work of Maynard and Aitken [6]. It should be emphasised that the primary elements can then be found in individual form or grouped in agglomerates or aggregates (dimension can then extend to some hundreds of nanometers).

A number of research projects have shown health effects related to nanostructured particles [7–11]. As a result, the prevention issues are high regarding nanostructured particles for health and safety at work

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**Notations**

| | |
|---|---|
| $a_p$ | Specific surface area of a particle ($m^2 kg^{-1}$) |
| $A_p$ | Surface area of a particle ($m^2$) |
| $A_{P,p}$ | Projected surface area of a particle ($m^2$) |
| $A_{P,pp}$ | Projected surface area of a primary particle ($m^2$) |
| $C_{ov}$ | Overlap coefficient (–) |
| $C_{ov,P}$ | Projected overlap coefficient (–) |
| $d_{pp}$ | Primary particle diameter (m) |
| $D_f$ | Fractal dimension (–) |
| $k_a$, $\alpha$ | Parameters of Eq. (12) (–) |
| $m_p$ | Particle mass (kg) |
| $N_{pp}$ | Number of primary particles (–) |
| $N(d_{pp})$ | Number size distribution of the primary particles (–) |
| $u$ | Statistical criterion (–) |
| $\rho_{pp}$ | Primary particle density ($kg\ m^{-3}$) |
| $\zeta_1$, $\zeta_2$ | Parameters of Eq. (7) (–) |
| $\phi$ | Parameter of Eq. (11) (–) |
| $\sigma(x)$ | Standard deviation observed on variable $x$ (unit of $x$) |

[12]. In this context, the measurement of occupational exposures constitutes one of the challenges to be tackled in the coming years [13,14]. Indeed, on account of the expansion taking place in the fields of nanomaterials and nanotechnologies, there are an increasing number of manufacturing, handling and transportation operations that can emit nanostructured particles liable to be inhaled. Furthermore, several toxicological studies have shown, for insoluble nanoparticles, evidence of surface area being a relevant dose metric [7,8,11].

However, there is no reference method that is stabilised and that can measure the surface area of airborne nanostructured particles (nanoaerosols).

At the present time, only the measurement of specific surface area by the BET method [15] constitutes a reference in the domain of materials and more recently in toxicology [16]. However, the low mass concentrations of nanoaerosols usually encountered (in the order of 0.1 $mg/m^3$ or less) are incompatible with the BET analysis, which requires at least samples of some milligrams.

Let us take as an example a nanoaerosol with a specific surface area of 100 $m^2/g$ present in the air at a mass concentration of 0.1 $mg/m^3$. This is sampled on a filter media at a flow rate of 10 L/min, which corresponds to a commonly used flow rate in occupational exposure measurements. The sampling duration of this aerosol allowing measurement of a surface area of 1 $m^2$, which corresponds to the detection limit of recent BET instruments, is thus 7 days, assuming a constant flow rate. It is clear that this duration is incompatible with taking aerosol measurements. Consequently, it is necessary to develop other techniques requiring a lower quantity of material that allow the determination of the specific surface area in the case of airborne nanostructured particles.

Electron microscopy, now entering into increasingly common use in the area of nanomaterial characterisation, is a technique offering a broad field of applications. Indeed, in addition to measuring the size of the primary particles and agglomerates observed, the images taken can be exploited with a view to characterising the structure of the particles, particularly by fractal analysis [17]. Their morphology is a fundamental data to describe the physical behaviour of these particles (transport, coagulation, deposition, physical–chemical properties).

A method to determine the specific surface area of nanostructured particles by transmission electron microscopy (TEM) is proposed in this work. It could be an interesting alternative to the BET technique, particularly as regards the particle mass required.

In this respect, nanostructured powders (a few hundreds of mg) of differing chemical natures, analysed beforehand by the BET method, were aerosolised under the effect of agitation and collected on a support allowing their observation by transmission electron microscopy (TEM grid). The images taken were then processed by a particular method to calculate the specific surface area of the nanostructured particles sampled. Both approaches should be equivalent if the particles do not present micro porosity and if placing them in suspension in aerosol form does not bring about segregation. In this work, five commercially-available nanostructured powders ($SiO_2$, $ZrO_2$, $Al_2O_3$, $Fe_2O_3$ and $Fe_3O_4$) were used with a view to testing and comparing the two methods.

## 2. Materials and methods

### 2.1. Description of the system

In order to determine the specific surface area from electron microscopy images, we produced the aerosols from different nanostructured powders. Powder aerosolization methods can be generally subdivided into three categories:

(1) fluidization by gas dispersion or ventilation in which the powder sample is (re)suspended by direct entrainment into airflow in a tube;
(2) "impact" method, in which the powder sample falls as a discrete slug through the air into or within an enclosed chamber, from which aerosol is sampled;
(3) mechanical dispersion or agitation (rotating drum and similar techniques), in which the powder sample repeatedly falls from top to bottom of a horizontal, rotating cylinder or tube and is entrained into airflow.

In our work, a vortex-type agitation has been chosen (Fig. 1). Within the vortex shaker, the aerosol is formed as a result of both a direct vigorous agitation of the nanopowder sample and a fluidization by the airflow across the nanopowder. This system is able to aerosolize a small amount of nanopowder (few tens of mg) and was designed to collect most of the airborne particles emitted via direct fluid entrainment of the sample to the measurement or collection device.

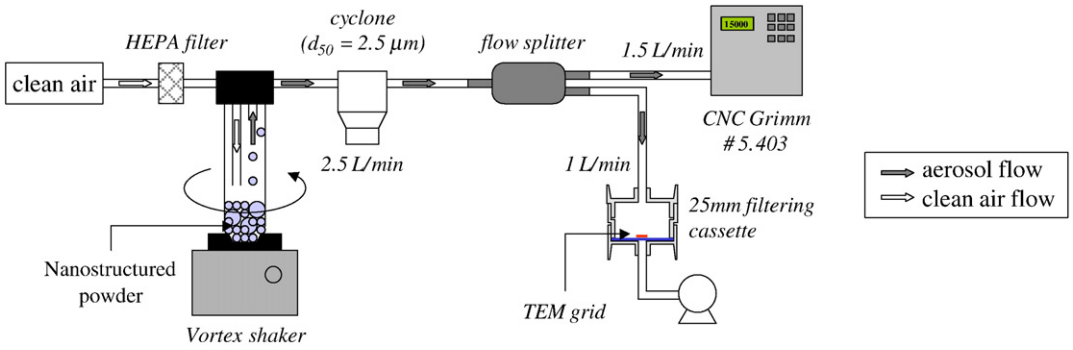


**Fig. 1.** Experimental set-up.