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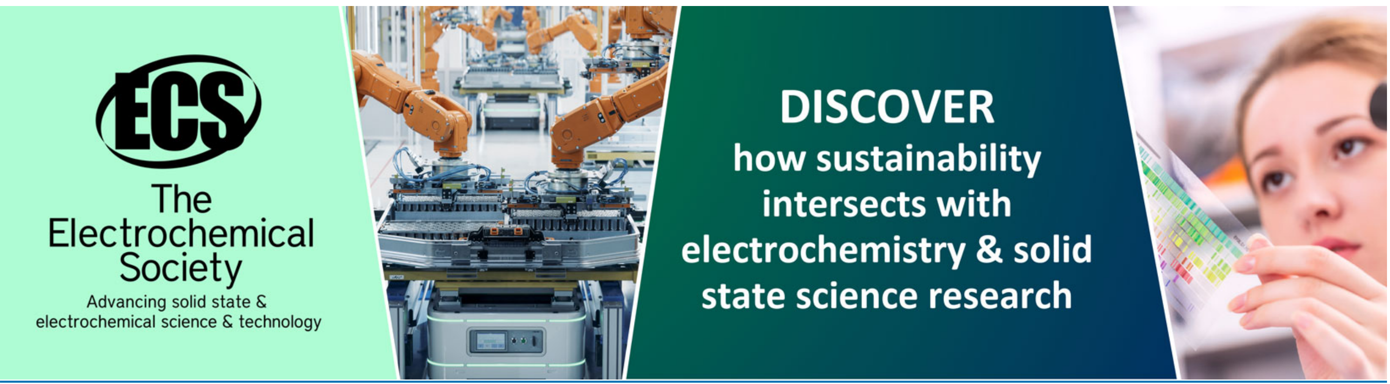

Airborne nanoparticle (Nanoaerosol) sampling efficiency analysis based on filtration on TEM grid

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Abstract. The scientific and technological issues associated with the characterization of the exposure of nano-aerosols is a huge technological challenge. Nano-aerosol measurement is a key point to characterize nanoparticle exposure. Transmission electron microscopy (TEM) coupled with energy-dispersive X-ray (EDX) is a comprehensive tool for determining size distributions and elemental compositions. Individual particle analysis allows the determination of size, morphology, specific surface, and elemental composition. Techniques allowing sampling on adapted analysis support TEM grids are of great interest to aerosol analysis: by using MPS and TEM analysis, sampling is directly and easily performed. The current paper explores the available theoretical models which assess sampling efficiency according to the chosen empirical approach. The recent studies which use this method are also briefly introduced.

1. Introduction

Nanoparticles are particles with at least one dimension less than 100 nm. For practical applications, in order to describe particle population quantitatively, it is necessary to obtain not only the mean particle size and the size distribution, but also more information for characterization such as elemental composition, exposure analysis [1]. Such data could be used for modeling purposes [2] and help design of safer materials [3]. Nanoparticles have a large surface area to volume ratio, which results in a high surface reactivity. As the concentrations of airborne nanoparticles increase with the development of nanotechnology and other sources, research focuses today also on potential negative impact of nanoparticles on human health. Nanoparticles are usually not removed from the upper respiratory tract, and mostly inhaled into the deeper areas. Nanoparticle exposure may thus cause numerous adverse health effects, such as cardiovascular diseases, heart disease and respiratory tract damage [4]. Furthermore, studies have shown relationship between nano-particle concentration in the urban environment or workplace and morbidity [5].

In order to meet different measurement objectives, lots of devices to characterize airborne nanoparticles have been introduced to the market. In general, there are two methods to characterize nanoparticles, collect nanoparticles on substances by different methods (e.g., filtration/diffusion/electric field…), followed by off-line analysis and monitor by (near) real-time and analysis that provide particle number concentration, mass concentration or surface area concentration directly. Even if lots of devices are developed, the most basic off-line method to measure the size of nanoparticles is the size analysis from the image using electron microscope, which could give particle size distribution and determine particle morphology. For example, in studies on the risks related to nanomaterials, electron microscope observation is a reliable method, and often the only way to verify the presence and form of aerosolized nanomaterials, and to distinguish between nanomaterials and background particles [6, 7].

TEM produces high resolution images and it is the most useful technique offering the possibility to both gain access to particle sizes and their elemental composition. Deposit particles on a support like a TEM grid can eliminate sample preparation which is time-consuming. TEM grids are round metal grids divided into hundreds of squares. In addition, TEM analysis of collected particles is energy-consuming. Some studies focus on direct nanoparticle collection, by filters on TEM grid. R'mili et al. [8] applied sampling technique by filtration using TEM grids which makes possible a relevant characterization of particles emitted during manipulation of carbon nanotube (CNT) powders. Fleury [9] characterized composite particles in a work environment around the extruder. Furthermore, sampling efficiency of different kinds of particles using this technique were studied by R'mili [10] and Ogura [11]. These researches showed that the new sampling technique is simple, low-cost and easy to use, both in the laboratory or practical applications.

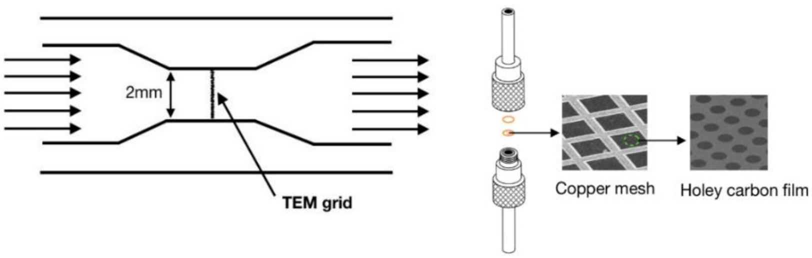

Figure 1. Concept diagram of the filter holder MPS and an aerosol particle collection system using a holey carbon film-coated TEM grid [11]

2. Theory sampling efficiency of filtration on TEM grid

According to the geometric characteristics, the TEM grids used for filtration are similar to a Nuclepore membrane and the "capillary tube model" is proper. Fleischer [12], Price [13], and their collaborators developed a type of filter material, a porous analytical filter trade-named Nuclepore. One developed theory named "capillary tube model" describes the Nuclepore filters best. The well-known capillary tube models developed in 1960-1970s were used to calculate the collection of particles by Nuclepore filters.

Spurny gathered a series of theories [14, 15] and developed a classical one [16]. The mechanisms by which particles are arrested in the Nuclepore filter have been identified. He modeled the overall collection efficiency of Nuclepore filters using separate terms for three classic deposition mechanisms: (1) diffusion to filter pore walls, (2) impaction, and (3) interception. The filtration properties of Nuclepore were determined and compared with an extension of Fleischer and Price's filtration theory. Smith [17] defined the relationship between particle size and collection efficiency. Then Manton [18] introduced a new term to explain diffusion to the filter surface, as shown in figure 1. After the 1970s, some researchers continued to improve the models. For example, Marre and Palmeri [19] took into account the effects of flow slip at the pore wall and expected to have higher efficiency in the intermediate crossover regime between Brownian diffusion and direct interception.

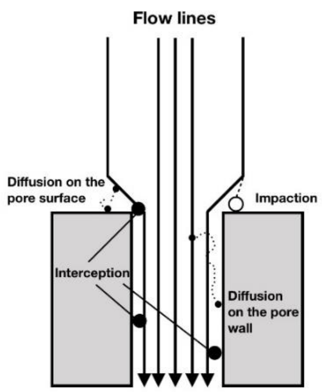

Figure 2. Schematic filtration mechanisms involved in separation on a capillary pore membrane [20]

2.1 Diffusion efficiency

Gormeley [21], Twomey [22] and Spurny's theory [16] demonstrated the diffusion deposition efficiency on the pore wall of filter, E_{Dw}, which were different expressions according to parameter N_D.

For the range $N_D < 0.01$, the diffusion efficiency was computed by the model of Gormley and Kennedy:

$$E_{Dw} = 2.56{N_D}^{2/3} - 1.2N_D - 0.177{N_D}^{4/3} \tag{1}$$

For $N_D > 0.01$, the equation of Twomey was used:

$$E_{Dw} = 1 - 0.81904\exp(-3.6568N_D) - 0.09752\exp(-22.3045N_D) - 0.03248\exp(-56.95N_D) - 0.0157\exp(-107.6N_D) - \cdots \tag{2}$$

Where N_D was defined as:

$$N_D = \frac{LDp}{{r_0}^2 U_0} \tag{3}$$

D is aerosol particle diffusion coefficient, L is filter thickness, p is porosity, U_0 is face velocity, r_0 is pore radius.

Smith [17] proposed that besides particles diffusion on the pore wall, filters can also collect particles by diffusion on the face of the filter, which was found to be the dominant mechanism for collecting particles by diffusion. Manton [18] also investigated diffusion of aerosols on the face of a Nuclepore filter with porosity in the range of 0.05 - 0.64. The diffusion efficiency on the filter surface E_{Ds} was:

$$E_{Ds} = 1 - exp\left\{-\frac{\alpha_1 \mathcal{D}^{2/3}}{[1 + (\alpha_1/\alpha_2)\mathcal{D}^{7/15}]}\right\} \tag{4}$$

where $\mathcal{D} = N_D/r_c U_0$, r_c is cylinder flow radius. $\alpha_2 = 4.5$, α_1 is function of porosity. In the range $0.05 \leq P \leq 0.64$, α_1 is adequately approximated by equation:

$$\alpha_1 = 4.57 - 6.46P + 4.58P^2 \tag{5}$$

2.2 Interception efficiency

Interception occurs when the center of a particle passes within the radius of the particle from the edge of the hole. If uniform flow is assumed, the interception efficiency E_R is expressed by Spurny [16]:

$$E_R = N_R(2 - N_R) \tag{6}$$

where $N_R = r_p/r_o$, r_p is particle radius.

If Poiseuille flow is assumed, E_R can be expressed by Smith [17] and Manton [23]:

$$E_R = [N_R(2 - N_R)]^2 \tag{7}$$

2.3 Inertial impaction efficiency

Pich's [24] work derived an expression for impaction efficiency E_I and made conclusions about the role of impaction in the mechanism of membrane ultrafilter action, which is the most used theory until now [16].

$$E_I = \frac{2\varepsilon_i}{1+\xi} - \left(\frac{\varepsilon_i}{1+\xi}\right)^2 \tag{8}$$

$$\varepsilon_i = 2Stk\sqrt{\xi} + 2Stk^2\xi exp\left[-\frac{1}{Stk\sqrt{\xi}}\right] - 2Stk^2\xi \tag{9}$$

$$\xi = \frac{\sqrt{P}}{1-\sqrt{P}} \tag{10}$$

$$Stk = \frac{mU_0C_c}{6\pi\eta r_0} = \frac{2C_cU_0{r_p}^2\rho_p}{9\eta r_0} \tag{11}$$

where Stk is Stokes number, m is the mass of a single aerosol particle, Cc is Cunningham slip correction factor [25-27], η is the dynamic viscosity of the flow, ρ_p is particle density.

So, the total sample efficiency E can be expressed as:

$$E = 1 - (1 - E_{DW})(1 - E_{DS})(1 - E_R)(1 - E_I) \tag{12}$$

3. Sample efficiency of filtration on TEM grid combined with experiment results

Experimental work has been carried out to determine collection efficiency of filtration on TEM grids. The most important ones are R'mili's [10] and Ogura's [11] works which also use constitutive models to calculate the collection efficiencies of holey carbon film-coated TEM grids.

In R'mili's study, the efficiencies of particle collection on TEM porous grids were evaluated. Two types of porous grids have been put to the test: the "Quantifoil" type and the "Holey" type. INERIS had developed a filter holder in order to meet this application, named MPS (Mini Particle Sampler), the internal structure of which is shown in figure 2. From 5 nm to 150 nm size range particles were collected, with a minimum efficiency of 15-18% around 30 nm. The experimental results greatly fitted the prevailing character of the diffusional deposition mechanisms under 30 nm, and impaction deposition mechanisms above 30 nm, as shown in fig.3. The physical model shows an increased efficiency on the small and large sizes. This study shows the filter holder MPS is a low-cost and easy tool to use.

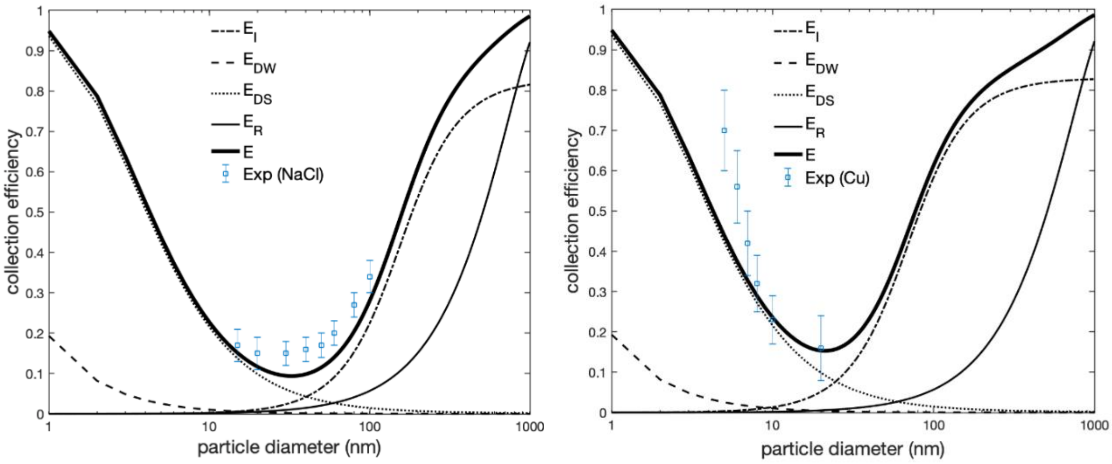

Figure 3. theoretical models compare with experimental collection efficiency of NaCl and Cu nanoparticles on Quantifoil 1.2/1.3, 400 mesh Cu TEM grid measured by R'Mili [10].

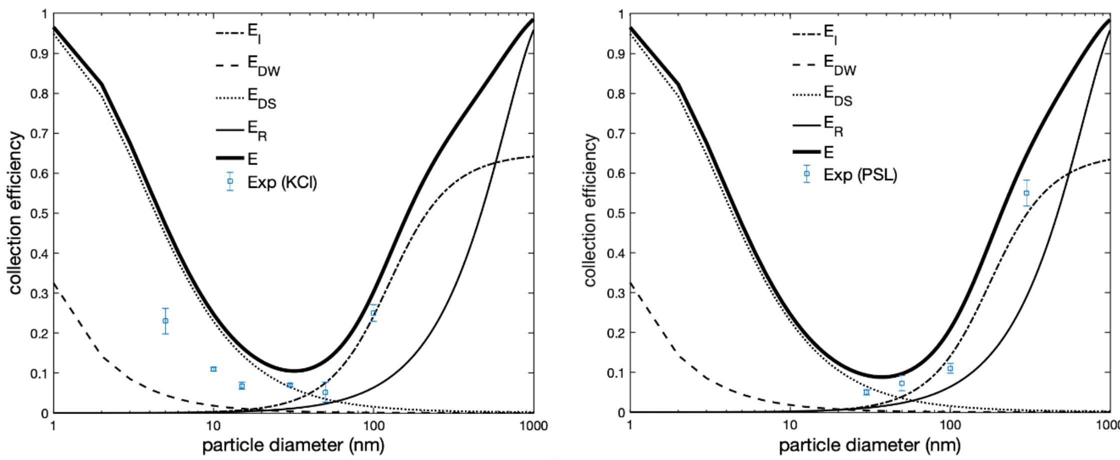

Figure 4. theoretical models compare with experimental collection efficiency of KCl and PSL nanoparticles on Quantifoil 1.2/1.3, 200 mesh Cu TEM grid measured by Ogura [11].

The same method was used by Ogura et al in 2014 [11]. The authors proposed a modified calculation method which considered the porosity of the copper mesh. Then the particle collection efficiencies on TEM grids both theoretically and experimentally were evaluated. Collection efficiency of two types of holey carbon grids, with nominal pore sizes of 1.2 and 0.6 μm, were tested separately. The overall collection efficiency of each grid and collection efficiency of the holey carbon film were determined. Physical model was compared with experimental results obtained in this study. The data showed that the theory overall collection efficiencies were consistent with the experimental overall collection efficiencies, which have a minimum efficiency about 5-9% around 15-30 nm, as shown in fig.4.

4. Conclusion

The work presented here shows that sampling of nanoparticles directly on TEM grids is a promising step for further analysis. The existing results shows the sampling efficiency is higher than 15%. Moreover, the theoretical models used for assessing the sampling efficiency show good agreements with experimental results using this method.

However, in the current researches, there may still remain sources of error. For example, in R'mili's set up, loss by deposition is due to the filter holder rather than the filtering medium. In Ogura's set up, measurement artifacts related to the use of two different counters upstream and downstream were observed. In addition, many influence factors such as pore size, flow rate, particle size which will influence nanoparticle sampling efficiency by TEM grid, should be taken into account. A modelling of the airborne particle concentrations deposed on a filtering medium could be a significant improvement to characterize an emission source of particles.

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