# MÉTHODE QUANTITATIVE DE CARACTÉRISATION DE LA MASSE À L'AIDE DE GRILLES TEM POUR L'ÉVALUATION DE L'EXPOSITION AUX PARTICULES SUBMICROMÉTRIQUES

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## TITRE

## QUANTITATIVE METHOD OF MASS CHARACTERIZATION USING TEM GRIDS FOR AIRBORNE SUBMICROMETRIC PARTICLE EXPOSURE ASSESSMENT

## RESUME

Le travail présenté ici vise à proposer une nouvelle méthode quantitative pour caractériser les concentrations massiques élémentaires par échantillonnage de particules et TEM - EDS. Le principe est de collecter les particules en suspension dans l'air sur une grille TEM poreuse, puis d'y ajouter une certaine masse de particules de référence, et de déterminer les pourcentages relatifs de tous les éléments via l'EDS. Les résultats montrent que les écarts absolus entre les rapports de masse élémentaire théoriques et les rapports expérimentaux restent inférieurs à 8%. Cette approche assure la sécurité, l'adaptabilité et la praticabilité lors de l'évaluation du risque d'exposition aux matières dangereuses.

## ABSTRACT

The work presented here aims to propose a new quantitative method to measure elemental mass concentrations via particle sampling and TEM-EDS. The principle is to collect airborne particles on a porous TEM grid, then add a certain mass of reference particles on it, and determine the relative percentages of all elements via EDS. Results show that the absolute deviations between the theoretical elemental mass ratios and the experimental ratios remain lower than 8%. This approach ensures safety, adaptability, and practicability when assessing the exposure risk of hazardous materials.

**MOTS-CLÉS:** quantification de masse, TEM-EDS, particule submicrométrique /**KEYWORDS:** mass quantification, TEM-EDS, submicrometric particle

## 1. INTRODUCTION

Nanoparticles and submicrometric particles are often released from commercial consumer products, which could present risks over their fate to workers and the environment (Bressot et al., 2017; Svendsen et al., 2020). The exposure assessment of such particles remains challenging because of their difficulties of sampling, measurement, and characterization (Schwaferts et al., 2019). It is crucial to know the released particles' characteristics, including the size, shape, number, mass, and composition. Transmission Electron Microscopy (TEM) coupled with related techniques such as Energy Dispersive X-ray Spectroscopy (EDS) is a high-resolution tool that offers a possibility of physical, chemical, morphological characterization, and single-particle analysis (Chen et al., 2005). The TEM grid-equipped Mini particle sampler (MPS) can be used to achieve the personal or static sampling of fine particles for the subsequent TEM characterization (R'mili et al., 2013). This sampling technique has turned out to be portable and easy to use (Bressot et al., 2018). It does not require energy-consuming tools, such as an electrostatic precipitator to prior charge particles (Fierz et al., 2015). The sampling efficiency of this technique has been improved and quantified through several studies (Xiang et al., 2021; Xiang et al., 2021). This technique has been employed in a wide range of applications such as occupational hygiene, consumer or environmental exposure assessment (Bressot et al., 2018; Morgeneyer et al., 2018; Zhao & Zhang, 2019).
Using this technique, the size, shape, number, and composition of airborne particles collected on the TEM grid can be observed and analysed by TEM and EDS. Combining real-time measurement instrumentation such as an SMPS, or an APS, the mass concentration can be obtained by calculation using mathematical models. However, during the calculations, the determination of the airborne particle density is a challenge (Buonanno et al., 2009). Moreover, the related real-time measurement technique in the workplace requires cumbersome and powered apparatuses. Another mass characterization method is to obtain time-integrated mass concentration by the gravimetric way (Methner et al., 2010) using an instrument such as Tapered Element

Oscillating Microbalance (TEOM). But the apparatus is also cumbersome and expensive (Topmiller & Dunn, 2013).
An easy method to obtain the mass information will better meet the characterization requirement. Compared with the previous methods, the present work proposes a specific characterization way for mass (concentration) of elements present in an unknown aerosol by collecting the tested aerosol and reference particles on one TEM grid and comparing the mass percentages of elements by EDS. The mass ratio of different elements (elemental mass ratio) was compared between the theoretical value and detection value. The mass of element on the TEM grid is independent of the temperature and humidity during analysis. Compared to the cumbersome on-line instruments, this new method appears to be very handy as only a short time of aerosol sampling in the workplace is usually needed.

## 2. MATERIALS AND METHODS

### 2.1. Materials and set-up

Three types of "Quantifoil" holey carbon film 400 copper mesh TEM grids (Agar Scientific) were used: 1.2/1/3, 2/2, and 2/1 for collecting particles. Two kinds of particles were deposited on the same TEM grid, one acting as reference material, the second acting as "unknown specimen" to verify the method by comparing theoretical elemental mass ratio and experimental ratio measured by EDS. Five kinds of airborne salt particles were used as potential reference materials or pseudo-unknown specimen: CsCl (purity: 99.5%), RbCl (purity: 99.5%), $SrCl_2$ (purity: 99.99%), $Ga(NO_3)_3$ (purity: 99.9%), and NaCl (purity: 99.5%).
An pseudo-unknown aerosol is sampled on a TEM grid, followed by the sampling of a reference aerosol on the same grid. The experimental design of the set-up for particle deposition is shown in Fig. 1. A membrane dryer generated clean, dry, and compressed air. Polydispersed aerosol was generated by spray drying salt solution using an atomizer (PALAS AGK 2000). Two silica gel dryers removed waterdrops, and the humidity was hence below 5%. The extra airflow was emitted through a HEPA filter. Monodispersed nano aerosols were produced by an electrostatic classifier (3082, TSI), which includes a neutralizer (3088) and a nano Differential Mobility Analyzer (DMA 3085 A). The aerosolized particles were neutralized by a radioactive source (TSI 3087) upstream of the filter. The neutralizer was utilized first to establish an equilibrium charge state on the particles, with known percentages of particles carrying no charge, single charge, and multiple charges associated with positive and negative polarities entering the DMA (Chen et al., 2018). Valves were utilized for inducing the flow to two symmetrically placed MPS, one with a TEM grid installed. The particle number were measured by a Condensation Particle Counter (CPC 3787, TSI). The particle number deposited on the TEM grid ($N_{\mathrm{deposition}}$) was calculated based on the particle counted numbers upstream ($N_{\mathrm{up}}$) and downstream ($N_{\mathrm{down}}$), measured by CPC in the conditions of without TEM grid, and with TEM grid, respectively.

$$N_{\mathrm{deposition}} = N_{\mathrm{up}} - N_{\mathrm{down}} \qquad (1)$$

The collection efficiency of the TEM grid *E* was calculated as:

$$E = 1 - \frac{N_{down}}{N_{up}} \qquad (2)$$

Ignoring the particle losses in the tubes, the particle number measured without the TEM grid is the number of particles generated from the atomizer. Particles with mobility diameters of 60-100 nm were deposited due to their higher sampling efficiencies (Xiang et al., 2021).

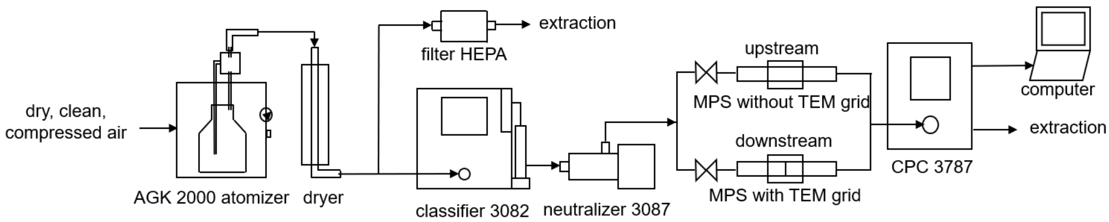


Figure 1. Concept diagram of the experimental set-up

### 2.2. Microscopical analysis

Particles collected on the TEM grids were analyzed by a Scanning TEM (STEM) performed on a JEOL JEM 2100F microscope with a Centurio silicon drift detector for ultra-fast atomic elementary maps. TEM provides micrographs with particle size, shape, as well as deposition distribution. EDS, measuring the average element percentage composition of a region, was performed by expanding the beam to cover a large grid area. The experimental mass ratio of reference element and element presents in the unknown aerosol is defined as the ratio of the mass percentages of those two elements measured by EDS. 21 squares uniformly located on the grid with a magnification of x20000 on the grid were analyzed. 15 min elemental mapping was carried out in each square to enable high precision. The TEM images were analyzed by the open-source program ImageJ (version 1.41 h) and origin pro-9.0 software (MA, USA, open source version) to get the particle size distribution.

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### 2.3. Determination of the theoretical elemental mass ratio

Besides the elemental mass ratio measured by EDS, the mass ratio of element present in the reference aerosol and present in the unknown aerosols was calculated for comparison and validity of the present method. The here so-called "theoretical elemental mass ratio" is hence defined as the ratio of masses of elements, i.e. reference devided by unknown. The mass of each present element, such as Rb on the TEM grid was quantified by the particle deposition number ($N_{deposition}$), particle size and shape, and element molar mass:

$$m_{\mathrm{Rb}} = N_{\mathrm{RbCl(deposition)}}{}^{*}\left(\rho_{\mathrm{RbCl}} * V_{\mathrm{RbCl}} * \frac{M_{\mathrm{Rb}}}{M_{\mathrm{RbCl}}}\right) \quad (3)$$

Where $\rho$ is the particle density; $M$ is the molar mass; and $V$ is the volume of a single particle.
Thus the theoretical mass ratio between different elements can be calculated easily.

## 3. RESULTS

### 3.1. Deposition of the reference particles

As equation (3) introduces, for quantifying the reference particle mass, particle deposition number and diameter are crucial information. Regarding to the particle number, results show reproducibility, repeatability, and stability of the particle deposition. The sizes observed by TEM are similar to those selected by DMA. 60 nm RbCl spherical particles are good references, as they remain non-hydrated, non-hygroscopic. Furthermore, Rb is a seldom present element and shows low toxicity. (The results have not been listed due to the word limit)

### 3.2. Experimental elemental mass ratio

STEM-EDS analysis was used to compare the percentages between two kinds of deposited elements and calculate the experimental elemental mass ratios. Representative result of EDS analysis in the conditions of depositions of RbCl and CsCl particles has been shown in this part. 60 nm RbCl and CsCl particles were deposited on a 1.2/1.3 TEM grid for 5 min, respectively. Fig. 2(a) and (b) are STEM images of square 8 before and after 15 min mapping. Comparing these two images, particles have not been destroyed after mapping. Particles showing a high dispersion in shape and size are observed on the carbon films but also at the hole edges. Fig. 2(c) and (d) show Rb and Cs mapping images. Both elements Rb and Cs are homogeneously distributed on the carbon film. Between 1-10 keV, two peaks of elemental Rb located at 1-2 keV and several peaks for the Cs element in the 2-6 keV range have been observed, as shown from fig. 2(e). Rb is a useful reference since that it has fewer spectra peaks. From quantitative data, the mass ratio of elements Rb and Cs is around 33:67.

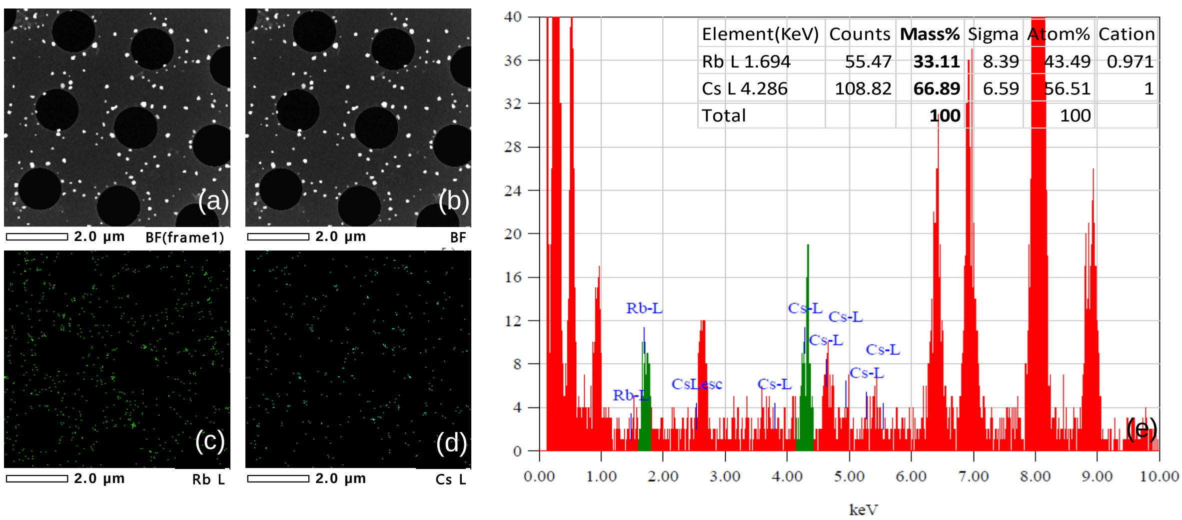


Figure 2. STEM images: before mapping (a), after 15 min mapping (b); EDS elemental mapping images of Rb (c), Cs (d); and spectra analysis with quantification results (e) of square 8

According to the quantitative analysis of the grid, the mass percentages of Rb or Cs are similar for 21 squares. The sample was approximately 46% of the Rb mass and 54% of the Cs mass. The standard deviation is 7.59%. The reference particles are proved to be homogeneously distributed on the grid.

### 3.3. Comparison between experimental mass ratio and theoretical mass ratio

The mass ratio of reference element and the element present in the "pseudo-unknow" aerosol was investigated for different couples of particles. The experimental mass ratio and the theoretical mass ratio were compared in the conditions of particle depositions of RbCl and another salt (CsCl, $Ga(NO_3)_3$, NaCl). The results of experimental and theoretical elemental mass ratios of those couples are shown in Table 1.

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Table 1. Comparison between the theoretical and experimental mass ratio of two kinds of elements

| Elements and size | Rb:Cs | | | | | | | Rb:Na | | | Rb:Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 60nm | | | | 100nm | | | 60nm | 100nm | | 60nm |
| Theoretical mass ratio | 32/68 | 21/78 | 38/62 | 35/65 | 35/65 | 37/63 | 38/62 | 26/74 | 36/64 | 31/69 | 54/46 |
| Experimental mass ratio | 25/75 | 25/75 | 46/54 | 42/58 | 30/70 | 43/57 | 31/69 | 33/67 | 37/63 | 33/67 | 55/45 |
| Absolute deviation (%) | 7 | 4 | 8 | 7 | 5 | 6 | 7 | 7 | 1 | 2 | 1 |

Table 1 shows that the theoretical elemental mass ratios are close to experimental ratios measured by EDS for all the tested conditions. Absolute deviations are lower than 8%. The aerosol deposition is turned out to be a proper way to characterize the mass of elements in the aerosol deposited on a TEM grid by adding a certain weight of reference element to the grid.

## 4. CONCLUSION

A method to quantitatively determine the mass of elements in particulate aerosol was developed by depositing it on a TEM grid and adding a certain mass of reference element to the same grid. The correlation of mass measured by EDS mapping allows for quantifying the elements in the unknown aerosol. Divers kinds of airborne particles were tested. 60 nm RbCl particles are good reference particles. Results show that reference particle deposition is easy to be achieved and the measured values such as deposited particle number are easy to be reproduced. X-ray analysis shows that the mass percentages of reference and test elements are similar over different squares of grid. For the tested conditions, the absolute deviations between the theoretical elemental mass ratios and the ratios measured by EDS are less than 8%.The consistency verifies that the proposed method turns out to be a proper way for determining the mass of element in the unknown aerosol, which is practicable for mass characterization in exposure assessment of particle emissions.

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