Morphological study of PM\textsubscript{2.5} by SEM-EDS in Ulaanbaatar

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Abstract. A morphological and elemental composition of PM\textsubscript{2.5} in air pollution of Ulaanbaatar by Scanning Electron microscopy (SEM) combined X-ray Energy Dispersive Spectrometry (EDS) were investigated. The morphological parameters were measured using the 5k magnification picture of SEM and analyzed the 752 individual particles of the 25 days (winter-10, summer-15) sample of the PM\textsubscript{2.5}. The size distribution shown the ~45% of particles were most harmful fraction of particulate matters for human health (less 0.4µm). These fraction particles increased up to 92% in winter. It was shown that ultrafine and irregular PM\textsubscript{2.5} results from the combustion. The results of determining the elemental composition of these individual particles are presented.

Keywords: PM\textsubscript{2.5}, Morphology and elemental composition, Size distribution, SEM, EDS

Introduction

The particulate air pollution is a growing problem in cities with emissions generating activities; these activities are mainly industrial and vehicular widely developed in large cities in different countries. Particulate also called aerosols air pollution is caused due to very small liquid and solid particles suspended in the air. They originate from a variety of stationary and mobile sources and may be directly emitted or formed in the atmosphere by transformation of gaseous emissions.

The use of Scanning Electron Microscope (SEM) has found application in the field of particulate air pollution for several years; its use has helped the study of particle morphology and single particles chemical composition. In fact, the simultaneous characterization of both physical-chemical and morphological parameters of a complex mixture of organic and inorganic particulate matter is one of the major aspects for the characterization and identification of emission sources that contribute to particulate concentrations in the atmosphere [1]. Size and chemical composition of ambient particulates strongly influence on human health, visibility and ecosystem etc.

Thus it is crucial to investigate the physicochemical characteristics of atmospheric particles and also to evaluate their potential toxicity. A large number of health-related studies recognized that fine particles particularly submicron sizes, penetrate deep into lung and exacerbate chronic respiratory and pulmonary diseases [2, 3]. Such diseases also induce morphological and functional alterations in human pulmonary epithelial cells [4]. Apart from this, elemental composition of particulate plays an important role in the chemical characteristics of particulate matters (PM) and provides interesting data, not only for the evaluation of its impact on human health, ecology and environment but also for the identification of specific emission sources [5].

The health effects of particulate emissions depend on the size of the particles. The larger particles emitted by cars do not find their way into the body as easily as the very fine particles emitted by laser printers. The smaller the particles, the more frequently adverse health effect on the entire organ system are observed. Ultrafine particles are classified as highly carcinogenic and are therefore especially harmful. According to studies, particles averaging 10 micrometers or less in size can adversely affect lung function, while particles smaller than 2.5 micrometers in size can trigger systemic diseases such as tumors or cardiovascular problems. The size of the particles is then the characteristic most studied in terms of classification and health damage. However, if other features such as the elemental
composition of the particle are considered the risk of health damage would probably be higher [6]. Specially, Particulate matter with aerodynamic diameters less than 2.5μm (PM2.5) has been found to cause health problems. It can trigger or exacerbate conditions, such as asthma, emphysema, and bronchitis, silicosis and lung cancer [7-9].

In this context, particles found in environment by the analysis of filters collected in area of the near to Ulaanbaatar city. For Mongolia’s air pollution level, annual mean of PM2.5 in the capital Ulaanbaatar city are 6-10 times higher than those considered safe by the WHO air quality guidelines [10]. Air pollution has become one of the most challenging issues in Mongolia, exacerbated during winter time because of solid fuel combustion. Especially, the capital city Ulaanbaatar where more than 47% of total population lives in is the most air pollution affected area in the country. In fact, during winter, Ulaanbaatar’s air pollution is caused by households and low pressure boilers burning raw coal in Ger district (80%); motor vehicle (10%); coal-fired power plants (6%); and solid waste and soil degradation (4%) [11,12]. In addition to be a large source of ambient air pollution, polluting fuels such as raw coal and biomass use for cooking and heating contribute to a significant additional burden to the health of the population from household air pollution [13].

As the development of tools for more precise characterization of atmospheric aerosols has been steady, as is the case for the use of electron microscope as the impact it has had the use of electrons, the study of particles, has been enormous, since it has allowed to obtain a vast information on the nature, origin and elemental composition of our object of investigation. The scanning electron microscope has sufficient specificity for the analysis of small particles and below the range of nanometers. Scanning microscope combines image of the particle morphology, i.e. shape, size, roughness, etc. as well as analytical information of the chemical elements that comprise the analysis of single atmospheric particles by Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM-EDS) is a powerful tool of recognizance emissions in urban places because the SEM may examine particles which are too small to be studied in the conventional optical microscope and also inform on the nature and origin of the particles revealed after the morphology, size and elemental composition [14-19].

The aim of this work is identification and characterization (morphology and elemental composition) of particles present in samples of PM2.5 as part of an air quality study by SEM-EDS in Ulaanbaatar.

**Sampling and analytical method**

Particles found in environment by the analysis of filters collected in atmospheric monitoring station property of the Nuclear Research Center, NUM in the City of Ulaanbaatar. The map shown in Figure 1 shows these locations. The station is located in the southeastern area of the city.

A PM2.5 particle was collected by GENT sampler, using a sampling flow of 16liter/min. Sampling was carried during 24 hour for two day in week. The filters used were polycarbonate, for collecting the aerosols samples polycarbonate nuclepore filters 47mm, 0.4μm pore diameters, were used. This type of filters media gives good results for morphological and dimensional analysis, in particular their pure composition and their flat surface let them suitable for the SEM analysis. Analyses of PM2.5 were performed using Hitachi SU8010 scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) in Inner Mongolia Normal University of China.

Specimens were processed by separating the collected particles in the polycarbonate filter which was placed over a sample holder, and is introduced into the chamber of SEM. The images of the samples were taken at a magnification of 1k, 2k, 5k, 10k, 20k, 40k, 45k and 60k. Then 5k magnification SEM images allow to analyses the elemental composition and morphological parameters of particles in the entire particle size range considered. Spectra of individual particles were obtained after scanning an electron beam with an accelerating voltage of 15 kV for determination of individual elemental chemical composition of the particles. Will be identified with EDS spectra the main chemical composition that make up the particles in the study area.

Those images are then elaborated with image analysis software Image-J®, for the dimensional of morphological analysis. Several morphological parameters were determined for PM2.5 classification. Count, area, length and perimeters measurements were automatically obtained using the software. All dimensional parameters were measured in calibrated units (microns).
Estimations were also made of equivalent spherical diameter (ESD), a commonly used parameter for particle sizing using following equation (Eq. 1);

$$ESD = 2 \sqrt{\frac{4\pi Are}{\pi}}$$  \hspace{1cm} (1)

We obtained the sphere and flake shapes and remaining is classified as part of the irregular of these. Irregular shape is no geometrical iconic particles. Thus is obtained three topical shapes.

**Results**

The average mass concentration of PM$_{2.5}$ samples in summer was found to be $\sim 52.96 \mu g/m^3$, in winter was found to be $\sim 101.29 \mu g/m^3$. The observed concentration is 2.2 and 4 times higher than the WHO standards ($25 \mu g/m^3$) and slightly higher than the MNS4585:2016 ($50 \mu g/m^3$) in summer, 2 times higher in winter. We obtained 480 SEM images of PM$_{2.5}$ particles (15 parts for each filter of 25 days samples) where its size and shape distribution, and elemental concentration of 639 each particles individually was analyzed by SEM-EDS.

Fig.2 shows that particles size distribution on the four size intervals established, indicated by percentages of the total analyzed particles. The size distribution results presented in the 2.95% of the particles identified $>1.8 \mu m$, 4.85% $1-1.8 \mu m$, 12.65% $0.8-1 \mu m$, 33.9% $0.4-0.8 \mu m$ and the remaining 45.3% less than $0.4 \mu m$. It is $\sim 45\%$ have been up to $0.4 \mu m$ which is the most harmful fraction of particulate matters for human health.
Fig. 2 Particles size distribution on the four size intervals established, indicated by percentages of the total analyzed particles, %.

Fig. 3 shows that Particles shape distribution on the 3 shape intervals established, indicated by percentages of the total analyzed particles. For the shape distribution, 55% - sphere of the total counted particles, 41% - irregular, and 4% - flake. Irregular shapes dominated in winter and sphere shapes dominated in summer, whereas flake shapes was no seasonal. This results shows that the summer PM pollution is sphere shape from the soil in summer and winter PM pollution is irregular from the combustion, based on the report of the air pollution study of Ulaanbaatar [17]. Irregular shape particles 2 times higher than taking into up to 0.4µm size particles increased to 92% in winter. It is indicates from the combustion that PM$_{2.5}$ is dominated by ultrafine size and irregular shape.

We obtained 752 particles of PM$_{2.5}$ particles where its chemical composition of each particle individually was analyzed by EDS. Fig. 4 indicates compositional data of elemental chemical constituents and counting percentage from PM$_{2.5}$ particles which showed the following elements: Na, Mg, S, Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr and Pb and the predominant elements were Mg, S, Ca, Fe and Al. Polycarbonate nucleapore filters consist of C and O; therefore those two elements were subtracted from loaded filters. Elemental analysis result shows the summer particles dominated by Na, Mg, S, Al, Cl, K, Ca, Ti and Fe. Whereas winter particles dominated by Si, V, Cr, Mn, Ni, Cu and Pb.
Fig. 4 indicates compositional data of elemental constituents and counting percentage in summer 512 and winter 240 individual PM$_{2.5}$ particles.

Conclusion

We investigated a morphological and elemental composition of PM$_{2.5}$ in air pollution of Ulaanbaatar by SEM-EDS. The SEM-EDS technique is a valuable tool for the characterization of PM especially for individual particles. The identification of the morphology and elemental composition of these particles provides valuable information for the determination of their origin and formation processes. The results of the size distribution shown the ~45% have been up to 0.4µm which is the most harmful fraction of particulate matters for human health. For the shape distribution, 55% - sphere of the total counted particles, 41% - irregular, and 4% - flake. Irregular shapes dominated in winter and sphere shapes dominated in summer, whereas flake shapes was no seasonal. This results shows that the summer PM pollution is sphere shape from the soil in summer and winter PM pollution is irregular from the combustion, based on the report of the air pollution study of Ulaanbaatar. These fraction particles increased to 92% in winter which is most of the irregular shape. It has been shown that ultra fine and irregular PM$_{2.5}$ indicates from the combustion. The results of determining the elemental composition of these individual particles are also given.

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