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Atmospheric Environment ▮ (▮▮▮▮) ▮▮▮–▮▮▮

ATMOSPHERIC ENVIRONMENT

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Transfer of a single particle for combined ESEM and TEM analyses

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Received 21 March 2003; received in revised form 11 July 2003; accepted 14 July 2003

Abstract

A new approach for transferring micrometer-sized particles between different sample holders has been developed using manipulators within an environmental scanning electron microscope (ESEM) sample chamber. Particles are transported from one sample holder to another using glass needles attached to manipulators, which allows a combination of microanalytical techniques for detailed analysis of specific particles. The technique was applied to airborne particles sampled in downtown Zurich, Switzerland. Initial, qualitative analysis of morphology and chemistry using the ESEM, led to the distinction of five particle classes. In order to investigate the structure of selected particles further, a specific particle was transferred to a transmission electron microscope (TEM) grid. The combination of analytical methods (ESEM-EDX and TEM) allowed us to characterize this particle in more detail and to identify its source. Thus, the approach presented here can be used to resolve the complex structure of single particles and to refine source apportionment based on single particle analysis.

Keywords: Electron microscopy; Airborne particles; Source apportionment; Morphology; Characterization

1. Introduction

Recent advances in analytical facilities enable highly sophisticated particle analysis (Jambers et al., 1996, 1995). Details of the morphology, chemistry and structure from single particles are now accessible using modern analytical techniques such as SEM/TEM-EDX (Buseck and Posfai, 1999; Li et al., 2003a, 2003b; Posfai et al., 1994, 1999), TEM-EELS/ESI (Mondi et al., 2002; Perret et al., 1995; Posfai et al., 2003), AFM (Kollensperger et al., 1998; Ramirez-Aguilar et al., 1999) or AFM-TEM (Posfai et al., 1998). These analytical developments applied to airborne particles improve our understanding of particle genesis, growth and alteration during transport in the atmosphere. Furthermore, the detailed characterization of single particles is important for an evaluation of their toxicity and allows an accurate source apportionment. The main motivation for such detailed single particle work arises from observed effects of particulate matter on human health.

Adverse health effects of airborne particulate matter are reviewed and documented in numerous recent papers (Anastasio and Martin, 2001; Anderson et al., 2002; Dockery et al., 1993; Peters and Pope, 2002; Pope, 2000; Pope et al., 2002; Schwartz, 1994). However, how particles interact with the human body remains a matter of debate. Several authors suggest that the composition of the surface layer of particles (sorbed trace metals or reactive gases, sulfuric acid, radicals) determines the toxicity of the particles (Amdur et al., 1988, 1986; Johnston et al., 2000; Richards et al., 1989). Other studies have demonstrated that the equivalent mass of small particles has a significantly more inflammatory effect on the lungs than larger particles (Johnston et al., 2000; Li et al., 1996; Oberdorster et al., 1992; Osier and Oberdorster, 1997). In summary, it is still unclear

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1352-2310/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S1352-2310(03)00574-0

whether the number of inhaled particles, the morphology, the surface chemistry and/or other physicochemical parameters is responsible for the toxicity of airborne particles.

Different analytical techniques often require different sample holders and thus multi-method investigations are performed on different particles, which can lead to erroneous interpretations. In this study, we present a methodology which enables the investigation of specific particles with environmental scanning electron microscope (ESEM) and transmission electron microscope (TEM). The technique involves transferring particles with manipulators in the ESEM from one sample holder to another. In this paper, we present results of a combination of ESEM-EDX and TEM analysis for a single particle.

2. Experimental/analytical

2.1. Sampling

Airborne particles were sampled directly onto 0.4 μm pore Nuclepore polycarbonate membrane filters. The sampling site was located next to an arterial road in downtown Zurich, Switzerland. A particulate air sampler (Partisol 2025, Ruprecht and Patashick), equipped with a PM10 inlet was used as a sampling device. The flow rate was 16.7 l/min. The sampling time was 5 h. The density of the particles on the filter is sparse and thus impact of particles on each other during sampling is unlikely.

2.2. ESEM

The ESEM technique is described in detail in Danilatos (1988, 1994). The major advantage of ESEM relative to conventional SEM is that non-conducting samples can be investigated without coating and that measurements can be made under controlled atmospheres. Hence, samples remain in their natural state during the ESEM analysis which is an important prerequisite for a multi-method investigation of specific particles. In this study, particles were exposed to ultrahigh vacuum conditions for subsequent TEM analysis and thus controlling the atmosphere in the ESEM was not critical. Although the ESEM can be operated under low vacuum and low acceleration voltage, specimen damage can still occur especially when analyzing beam-sensitive particles. Thus, radiation damage constrains our approach to particles which are stable under the electron beam in the ESEM.

In this study an ESEM-FEG XL30 (FEI) was used at of 15 kV acceleration voltage and 10 mm working distance. The chamber pressure was set to 1.2 Torr. $H_2O_{(g)}$ was used as imaging gas. A gaseous secondary electron detector (GSED-Large Field Detector) was used for image formation. Best results were achieved when particles were sampled on a conducting substrate. Hence, filters were coated with a thin layer of carbon (6–8 nm) prior to sampling. For elemental analysis of the particles, an EDX system (EDAX) attached to the microscope was used.

2.3. Transferring of particles using manipulators

Different microanalytical techniques have specific requirements with respect to sample preparation and sample holder. The combination of different analytical techniques for a single particle requires that the particle of interest can be transferred from one sample holder to another. In this study, transfer was achieved using manipulators.

Two manipulators equipped with fine glass needles are placed within the sample chamber of an ESEM (Fig. 1). The manipulators are attached to the chamber door to allow independent movement of the stage. The procedure of transferring particles starts with an accurate positioning of the manipulator-tips before closing the ESEM sample chamber. For this purpose an optical microscope with standard magnification 600 × is attached to the ESEM chamber door. It simulates the field of view in the ESEM and its focal length corresponds to the working distance of the ESEM. Once within the sample chamber, the movement of the needle tips can be observed directly within the electron microscope.

The manipulators are remote controlled and can be operated under high vacuum, although we used low-

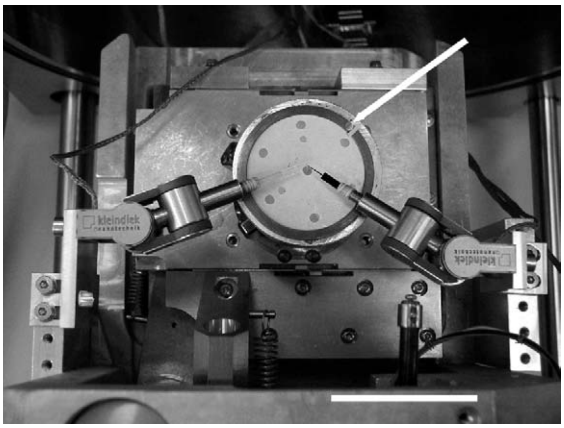

Fig. 1. Manipulators within the ESEM-sample chamber. The stage with Nuclepore filter and TEM-grid (white arrow) moves independently from the manipulators. The glass tip of the right manipulator is highlighted in black for better visibility. The movement of the needles is defined by one linear and two rotational axes. Scale bar is 5 cm.

vacuum conditions for this study. Three piezo-driven motors allow a fine needle attached to the manipulators to be moved in one longitudinal and two rotational directions. Detailed technical information about the manipulators is given in Kleindiek et al. (1995). The minimum step size is 2 nm. However, in practice the accuracy and precision of movements are limited by factors such as the coarseness of the needle tip, the resolution of the electron microscope and the physical interactions between the needle and the particle.

Various types of needle can be attached to the manipulators. Tungsten needles are available commercially with tip diameters as small as 100 nm (Micromanipulator Co., Inc). Fine glass tips with a diameter of less than 100 nm can be prepared from glass capillaries using a micropipette puller. We fabricated the needles using a PC10 Puller (Narishige) from boron silicate glass rods.

According to the experimental needs, tip materials with suitable physical properties can be chosen. Best results for our purpose were obtained using fine glass tips. The high elasticity of glass needles makes them more durable and they withstand deformation. Glass needles exhibit good adhesion properties, and specific particles grabbed from the Nuclepore filter adhere to the needle until placed on a suitable sample holder for subsequent analysis. The transfer of particles from one sample holder to others causes mechanical stress on the particles. However, as the transfer can be observed in the ESEM, any damage to the particle, such as breaking or deforming, would be noticed. In our experiments damage was not observed. Thus, we conclude that the forces, which keep the aggregates together overweight the forces caused by the manipulators.

2.4. TEM

A TEM (FEI CM30, source LaB6) was used to investigate single particles at high magnification. An acceleration voltage of 200 kV was applied. Carbon-coated, copper TEM grids were used in combination with a single tilt sample holder. The TEM was operated in bright field mode.

3. Results

Five different particle classes were distinguished based on morphological and chemical information obtained with the ESEM-EDX. The classes are described in detail below. A source apportionment of class 5 particles required additional information about the internal structure of the particles. We present an example of a multi-method investigation of a single particle of class 5, which was transferred to a TEM grid for subsequent analysis.

3.1. Particle classes

Class 1: Class 1 particles are typically round and prone to beam damage. The elemental analysis of class 1 particles shows only potassium, in addition to carbon and oxygen from the Nuclepore filter. Potassium is considered to be a marker for biological material (Liu et al., 2000; Silva et al., 1999). The susceptibility to radiation damage also is typical for biological material (Isaacson et al., 1973). Based on these two characteristics class 1 particles are allocated to a biological source.

Class 2: Particles of class 2 are almost perfect spheres. Their elemental shows only iron and oxygen. The perfect spheroid shape is indicative of combustion or other high-temperature processes (Conner et al., 2001).

Class 3: Particles of class 3 have an angular shape and are up to several microns in diameter. Major components of these particles are iron and oxygen. The angular shape and size of these particles is indicative of mechanical abrasion products.

Class 4: Class 4 particles are angular fragments. The analysis shows silica, aluminum and/or calcium as the most abundant elements, which is typical for mineral components (silicates, carbonates, etc.). Shape and chemistry of these particles indicates that they originate from mechanical abrasion of geological material.

Class 5: These particles have an irregular shape with a diameter of a few microns. They are composite, consisting of numerous smaller particles. A representative image of a particle of this class is given in Fig. 2. Elemental analyses revealed that iron is a major element. However, based on morphological criteria and EDX

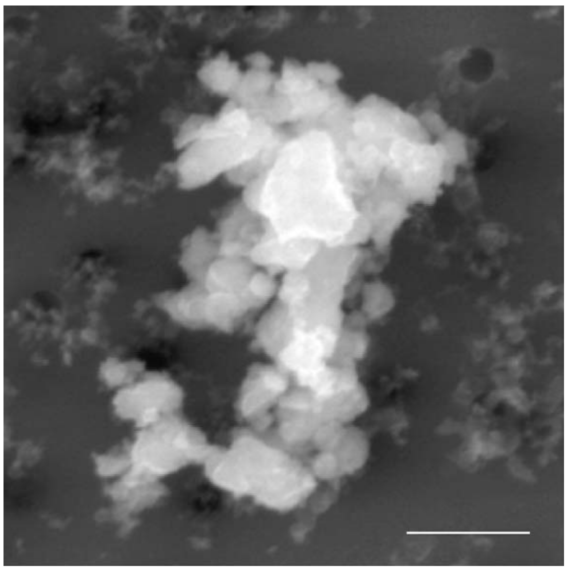

Fig. 2. SE-image of class 5 particle . The particle is irregularly shaped and iron bearing. Scale bar is 1 μm.

analysis these particles cannot be assigned to a specific source.

3.2. Detailed analysis of class 5 particles

For subsequent analysis in the TEM a particle of this class was transferred to a TEM grid using the manipulators. The TEM grid was placed at the edge of the ESEM stage (Fig. 1). The needles of the manipulators were positioned directly above the particle. The stage was raised until the needle touched the particle. When the particle stuck to the needle, the stage was lowered and moved until the TEM grid was in the field of view (Fig. 3). Then the stage was raised again, until the tip of the glass needle with the attached particle touched the carbon coating of the TEM grid. This caused the particle to bounce off the needle and stick to the carbon coating. The position of the particle on the TEM grid was memorized for relocation within the TEM.

As seen in Fig. 2, class 5 particles have a diameter of a few microns and an irregular shape. Results from the analysis within the ESEM already revealed that these particles represent agglomerations of numerous nanospheres. Under low magnification in the TEM (Fig. 4) it can be seen that the transferred particle (4–6 μm) consists of numerous microdomains with diameters in the range of 0.5–2 μm. The dark cores of these microdomains are too thick for electron transmission. Electron-transparent regions were found between microdomains and at their edges. Information from bright-field imaging in TEM revealed the internal structure of the particle, and was complementary to the morphological information obtained from ESEM.

Images taken at higher magnifications (Fig. 5) showed the packing and arrangement of single nanospheres. These nanospheres have uniform diameters between 10

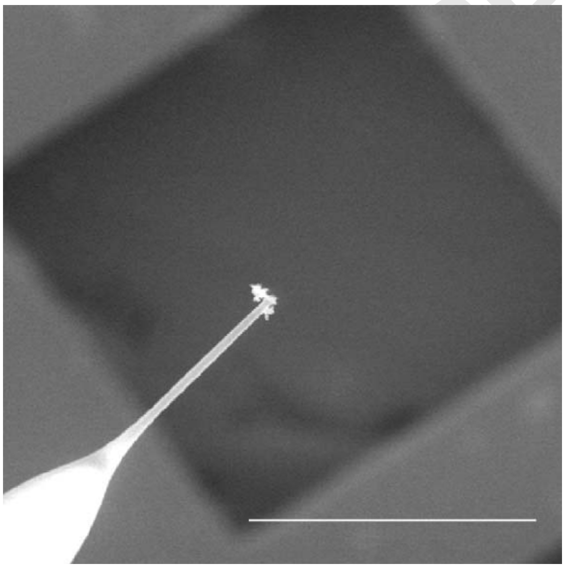

Fig. 3. Glass needle with the attached particle above the carbon coated TEM grid. Scale bar is 50 μm.

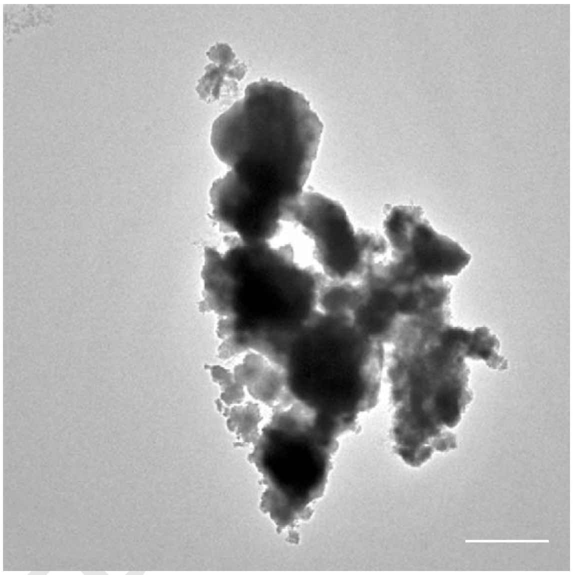

Fig. 4. TEM bright field image showing an overview of the class 5 particle. The entire particle (4–6 μm) consists of several agglomerated microdomains (0.5–2 μm). Scale bar is 1 μm.

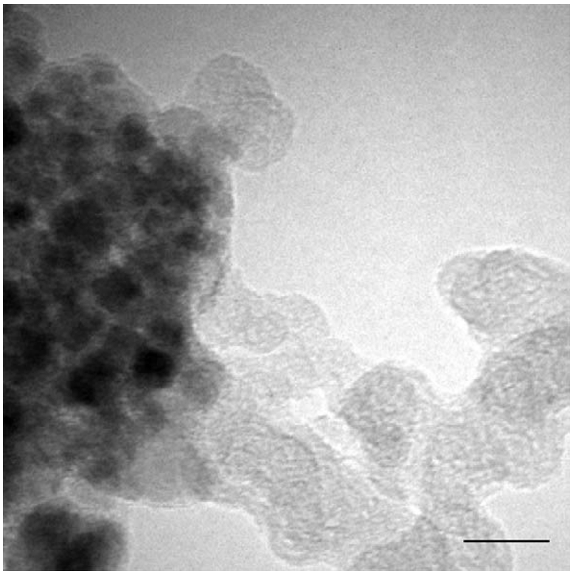

Fig. 5. TEM bright field image showing structural detail of class 5 particle. The image shows agglomerated nanospheres with a diameter of 10–30 nm. The nanospheres are interpreted as primary soot particles resulting from gasoline or diesel combustion. Scale bar is 20 nm.

and 30 nm, which corresponds well with other TEM studies of soot particles (Posfai et al., 2003; Shi et al., 1999, 2000).

The entire particle can thus be described as an agglomeration of nanospheres, which form microdomains similar to soot aggregates described in numerous papers (Buseck et al., 2000; Katrinak et al., 1993; Li et al., 2003a; Posfai et al., 1999, 2003). The ESEM-EDX spectra obtained from the core of the microdomains revealed that the dense core mainly consists of iron.

4. Discussion

Based on the morphological and chemical information from ESEM, particles of class 5 appear as agglomerations of submicrometer particles. The cores of these agglomerations are iron-rich and are covered with smaller particles. For a source apportionment more detailed information about the structure of the smallest constituents covering the iron core is necessary.

TEM bright field images revealed that the smallest constituents have a uniform spheroid shape with diameters in the range of 10–30 nm. These nanospheres have dimensions which are typical for primary soot particles resulting from gasoline or diesel combustion (Ristovski et al., 1998; Shi et al., 1999).

Based on the complementary information obtained from TEM analysis, the particle structure can be described over three scalar orders, resulting in different constituents at each scale: nanospheres, microdomains and the entire particle. Primary soot-nanospheres agglomerate, and form secondary microdomains. Iron-rich nuclei in the core of the microdomains may act as seeds for agglomeration. The entire particle comprises about 20 of these microdomains.

High iron content of particles is characteristic for traffic emissions. For example, Pakkanen et al. (2001) compared the compositions of atmospheric fine and coarse particles at rural and urban sites. The higher iron content at the urban site was attributed to local traffic. In a tunnel study, Sternbeck et al. (2002) determined metal emissions from the road traffic. Iron-rich particles were possibly emitted directly from the vehicles, although high concentrations of iron result from resuspension within the tunnel.

Due to the close association of the iron cores and combustion related nanoparticles within particles of class 5, they were assigned to a local road traffic source. This is consistent with the high traffic density at the sampling locality (close to a busy road). The agglomeration of combustion nanoparticles and iron cores could have taken place within the exhaust pipe or later in the atmosphere. Possible sources for the iron particles are resuspended material or road traffic emissions. In the present study, the investigation of a single particle was performed manually. Thus, no statistical information about the relative abundance of the different particle classes is available. For further refinement of source apportionment and a better understanding of health effects of airborne particles it will be necessary to combine specific particle information with statistical data. Numerous studies have already shown advantages of automated particle analysis (Conner et al., 2001; Katrinak et al., 1995; Raeymaekers et al., 1984; vanMalderen et al., 1996; Xhoffer et al., 1991) whereby size, shape, morphology and chemical composition of a large number of particles is determined. Based on this data different particle categories can be defined and quantified. Transferring particles using manipulators offers a new way to combine this data with more sophisticated single particle analysis. Specific particles which have been identified as representative for a certain particle category (based on automated particle analysis) can be further investigated with more sophisticated techniques such as TEM-EELS/ESI and AFM.

5. Conclusion

In this study, a methodology has been developed for combining different microanalytical techniques for investigation of a specific particle. For this purpose a micrometer-sized particle was transferred to suitable a sample holder using manipulators within the ESEM.

To illustrate this procedure, we used airborne particles sampled on a Nuclepore filter. Firstly, different particle classes were determined based on morphological and chemical criteria within an ESEM. Particles of one class showed a complicated morphology and it was impossible to assign them to a specific source. Thus, a representative particle of this class was transferred to a TEM grid using manipulators. TEM investigations revealed more detailed information about the internal structure of this particle. It has soot-like nanoparticles agglomerated on iron-rich cores that form microdomains. The entire particle consists of several of these microdomains. The complementary information from ESEM and TEM is consistent with a local road traffic source of this particle. This example documents the potential of multi-method investigations of single particles. Instead of finding different particle types during laborious TEM analysis, classification can be done in advance by (E)SEM, where an automated particle analysis can be used. The presented method generally allows the investigation of a single particle with different analytical techniques—not just ESEM and TEM—which provides comprehensive data about single particles and thus enables a very accurate source apportionment.

Acknowledgements

This project was funded by the Swiss Federal Laboratories of Materials Testing and Research (EMPA). We thank S. Kleindiek for technical support regarding the installation and use of the manipulators. Finally, we thank T. Semeniuk for critical review and English revisions.

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