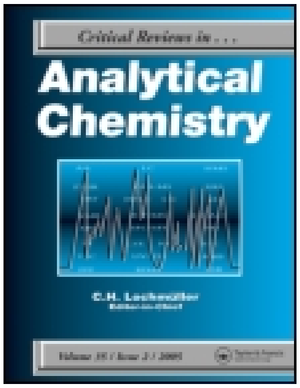

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/batc20

The Progress in Electron Microscopy Studies of Particulate Matters to Be Used as a Standard Monitoring Method for Air Dust Pollution

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To cite this article: Przemysław Sielicki, Helena Janik, Agnieszka Guzman & Jacek Namieśnik (2011): The Progress in Electron Microscopy Studies of Particulate Matters to Be Used as a Standard Monitoring Method for Air Dust Pollution, Critical Reviews in Analytical Chemistry, 41:4, 314-334

To link to this article: http://dx.doi.org/10.1080/10408347.2011.607076

Critical Reviews in Analytical Chemistry, 41:314–334, 2011

ISSN: 1040-8347 print / 1547-6510 online
DOI: 10.1080/10408347.2011.607076

The Progress in Electron Microscopy Studies of Particulate Matters to Be Used as a Standard Monitoring Method for Air Dust Pollution

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The present article reviews studies on air solid particles carried out with the use of electron microscopy. Particle analysis combining scanning and transmission electron microscopy (SEM and TEM) can be used to derive size-resolved information of the composition, mixing state, morphology, and complex refractive index of atmospheric aerosol particles. It seems that electron microscopy is more widely used in atmospheric particulate matter analysis, but the usage of this method is sometimes problematic. First of all, there is no standard methodology adapted for dust analysis, and it is difficult to compare the results coming from different laboratories. Nevertheless, it was shown that this method has potential to be used in the future as a standard monitoring procedure of air solid particles.

Keywords PM, particulate matter, atmospheric particulate, air particle analysis, EDX, EDS, scanning electron microscope, transmission electron microscope, SEM, TEM

INTRODUCTION

In recent years there has been increasing interest in atmospheric aerosols. Nowadays, a wide range of analytical techniques is used for aerosol analysis, where an extensive spectrum of their properties is determined. Atmospheric particulate research is undertaken to determine particulate matter harmful to human health and its impact on the natural environment. Studies are also carried on for particulate matter source estimation or testing. Moreover, particulate analysis is essential to dust removal system design.

Electron microscopy allows simultaneous single particle observation, obtaining information about its elementary composition (so-called chemical analysis of single particles), and computer image analysis. It is an innovative method in air particle analysis, considered more and more often in the literature as a desired standard method. Hereafter, it is to be considered along with present atmospheric particulate matter analysis methods (weight analysis, liquid chromatography, inductively coupled plasma-mass spectrometry (ICP-MS)).

Individual particle analysis combining scanning and transmission electron microscopy (SEM and TEM) can be used to derive size-resolved information of the composition, mixing state, morphology, and complex refractive index of atmospheric aerosol particles (Kandler et al., 2007). In the literature most often research teams classify particulate matter based on particulate spectral composition and its characteristic morphological features.

The present article reviews studies of solid particles carried out with the use of electron microscopy to show that this method could be introduced as a standard monitoring procedure, complementing the standard weight monitoring method.

PARTICULATE MATTER

Particulate matter (PM) is composed of inert carbonaceous cores with multiple layers of various adsorbed molecules including metals, organic pollutants, acid salts, and biological elements such as endotoxins, allergens, and pollen fragments (Gualtieri et al., 2009). This term refers to the solid and liquid particles (dust-size pollutants) that are dispersed into ambient air (Vallius, 2005). Particulate matter contains organic (soot, polycyclic aromatic hydrocarbon (PAHs)) or inorganic compounds (metals, sulfates, nitrates, and other inorganic species),

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or combinations of both organic and inorganic constituents (Sondreal et al., 2004). It can be classified into *primary* and *secondary* particles based on the mechanism of their formation (Vallius, 2005). PM may be emitted directly (primary PM) or be formed in the atmosphere (secondary PM) (Sondreal et al., 2004; Sillanpää, 2006). Both types of particles are subject to growth and transformation, since there can be formation of secondary material on the surface of existing particles.

Primary aerosols, often larger than 1 μm, are emitted directly into the atmosphere and include sea salt, mineral dust, volcanic emission, fly ash, and biogenic particles (Krejci et al., 2005).

Secondary particles are formed from gases through chemical reactions in the atmosphere involving atmospheric oxygen (O_2) and water vapor (H_2O); reactive species such as ozone (O_3); radicals such as the hydroxyl (OH) and nitrate (NO_3) radicals; and pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and organic gases from natural and anthropogenic sources. The particle formation process includes nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere, condensation of low-vapor pressure gases on existing particles, and coagulation of particles. Thus, any given particle may contain particulate matter (PM) from many sources (Krejci et al., 2005; Wilson et al., 2002). Secondary particulate matter can be classified into three parts: sulfur-containing compounds, nitrogen-containing compounds, and organic compounds (Sillanpää, 2006). These particles can be classified by their physical size; the size is from a few nanometers (nm) to tens of micrometers (μm) in diameter (Vallius, 2005). The majority of the secondary produced particles are in the sub-micrometer range (Krejci et al., 2005).

The investigation of primary aerosol sources, especially for soot, and their interaction with secondary aerosols has currently received attention due to their impact on radiative forcing and global climate change (Ketzel et al., 2004).

SOURCES OF PARTICULATE MATTER

The composition and mass concentrations of fine aerosol particles in clean background areas are strongly affected by long-range transport. During transport and aging, particles of different origin may change their properties due to coagulation and cloud processes as well as due to reactions with gases via various heterogeneous pathways (Niemi et al., 2006).

Depending on the aerosol properties and meteorological conditions, the residence time of aerosol particles in the atmosphere ranges from hours to weeks (Sillanpää, 2006). The horizontal distribution of aerosol concentrations in urban areas varies over a large range, depending on the proximity of emission sources (their geographical location, season of emission, and meteorology) as well as on atmospheric stability and the mixing height (Sillanpää, 2006).

There are two origins of PM emission. Atmospheric particles can be emitted from natural sources such as sea spray (sea salt), crustal erosions, volcanic emissions, dust outbreaks, soil-related dust, and biogenic particles including bacteria, fungal spores, and pollen (Perrone et al., 2006). However, most particulate matter is formed due to human activity, so it is from an anthropogenic source. The main starting places of these particles are different combustion processes, including diesel and gasoline vehicles, biomass burning, industrial activities, energy production and various special activities, and from different mechanical processes (Vallius, 2005; Sillanpää, 2006). Particulate matter from these origins is partly released as fugitive emissions, which are not collected and released in a controlled manner, but emitted from a variety of points and areas connected to a process (Vallius, 2005).

The most significant stationary combustion PM sources include energy production facilities such as municipal power plants, waste incineration, and residential combustion. Several industrial processes, such as iron and steel production, also involve combustion of fossil fuels or biomass for generating power and heat needed for the process. Most of these sources are considered point sources, although smaller and more widespread sources such as residential combustion could also be considered as an area source. Physical and chemical characteristics of the particles emitted from these origin categories depend on the combustion process itself and the type of fuel burned (solid, liquid, or gas) (Vallius, 2005). Therefore, diesel and gasoline vehicle emissions are major sources of PM with a diameter range < 100 nm (UFPs, ultrafine particles) in urban environments and usually consist of solid soot aggregates coated with an adsorbed hydrocarbon and sulfate layer, volatile organic and sulfuric acid droplets, and ash (Barone and Zhu, 2008).

Although anthropogenic sources of atmospheric particles are globally smaller producers of aerosol particles than natural sources, they are strongly concentrated in industrialized regions. Combustion particles, generated during incomplete combustion of fossil fuels and biomass, consist of tens to thousands of primary carbon particles (diameters $\approx$ 20–50 nm), leading to a large surface area per mass (Kocbach et al., 2006).

Differences in sources and in meteorological conditions may strongly affect composition, mixing state, concentration, and size of different particle types observed. These are essential factors related to the environmental and health impacts of aerosols, such as climate change and transport of nutrients, acids, and toxic compounds (Niemi et al., 2006). With complicated and multiple emission sources, individual particle characterization of sources and receptor samples has become a necessary means for accurate source apportionment (Shi et al., 2003).

HEALTH AND ENVIRONMENTAL RISKS OF PARTICULATE MATTER

Research on the effects of particulate matter on human health was initiated in the 1970s (Ferris et al., 1979) and has been strongly developed since then. Numerous studies (Pope and Dockery, 2006; Dockery et al., 1993) conducted within the past several years suggest that these small particles cause serious problems to human health, contributing to increased mortality and sickness (Shi et al., 2003; Mastalerz et al., 1998; Lorenzo et al., 2006). The mechanisms underlying these adverse effects are not well understood, and major questions concerning the specie size fraction, chemical composition, and causative mechanisms leading to the observed health effects remain (Sondreal et al., 2004; Kocbach et al., 2006; Diociaiuti et al., 2001). This is partly due to results from epidemiological surveys showing that there is a correlation between the mass concentration of particles and mortality and hospitalization (Ketzel et al., 2004).

From a health perspective, the size of the particles is important as it affects their ability to penetrate into the lungs and cause adverse health effects. The larger particles (e.g., those greater than 10 microns) tend to settle in the nose and mouth and are unlikely to pose a health risk (Carbon, 2003). However, ultrafine particles (i.e., diameters less than 0.1 μm) are considered especially detrimental to human health, since these particles can be inhaled and deposited deep in the alveoli of human lungs (Ketzel et al., 2004). It has been increasingly recognized through epidemiologic investigations that particulate matter in agricultural air contributes to the progression and exacerbation of respiratory diseases (such as asthma and other ailments), and in urban air leads to an increase in morbidity and mortality from respiratory and cardiac conditions (Mueller-Anneling et al., 2004). Children's susceptibility to health problems as a result of exposure to air pollution is of concern. Children may receive an increased dose of particulate matter to their lungs compared to adults (Wheeler et al., 2000). Moreover, PM has been linked to cancer and premature death (Monahan, 2003).

The investigation of primary aerosol sources, especially for soot and their interaction with secondary aerosols, is currently receiving attention due to their impact on radiative forcing and global climate change (Ketzel et al., 2004). Recent reviews of the adverse effects of diesel exhaust particles associate both the carbon particle core and the adsorbed organic compounds with the observed immune responses (Kocbach et al., 2006). An increasing number of studies have implicated transition metals as possible mediators of particle-induced airway injury and inflammation. Iron and other ionizable metals with labile or vacant coordination sites may initiate lipid peroxidation through production of oxygen-based free radicals (Frampton et al., 1999).

Knowing that aerosols are important atmospheric constituents on local, regional, and global scales, exposure to PM is correlated with increased human mortality and particles influence the Earth's climate system.

Particulate matter influences climate directly by absorbing and scattering incoming solar radiation, and indirectly by acting as cloud condensation nuclei (CCN) and ice nuclei (IN), thereby affecting cloud microphysical and optical properties, as well as precipitation rate and lifetime of clouds (Johnson et al., 2005; Gerasopoulos et al., 2007; Sun and Ariya, 2006). All influence the radioactive balance of the earth's atmosphere (commonly referred to as the *indirect effect*) (Pierce and Adams, 2007). Moreover, due to the spatial and temporal heterogeneity of aerosol occurrence and properties, PM causes visibility impairment in urban areas (Walgraeve et al., 2010). Thus, increased effort in characterizing tropospheric aerosols is needed to reduce uncertainty in the aerosol forcing estimate (Mihalopoulos et al., 2007) of high mass concentrations of fine particles. PM components/parameters such as particle number, morphology, particle size distribution, PM mass, ions (sulfate, nitrate, and ammonium), strong acidity, elemental carbon (EC), total organic carbon (TOC), metals, toxic elements, crustal elements, particle density, bulk chemical composition, trace element content, strong acid content, and sulfate content need to be measured (Wilson et al., 2002; Harrison and Yin, 2000).

ANALYTICAL METHODS USED FOR AEROSOL DETERMINATION

In the present article methods of solid particle analysis with the use of electron microscopy are discussed. Other analytical methods in the examination of atmospheric aerosol are given in Table 1 and are described more widely in McMurry (2000) and Wilson et al. 2002.

ELECTRON MICROSCOPY

Electron microscopy encompasses a family of analytical techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), each with its associated strengths and limitations (Casuccio et al., 2004). An electron microscope is similar in design to an ordinary light microscope with one key difference: instead of using light, it uses *electrons*. Using a cathode ray tube or filament (a source to generate highly excited electrons) in a vacuum, electrons are accelerated toward a given specimen by creating a potential difference. TEM uses transmitted electrons that can penetrate the sample. Obviously this sample must be very thin, since conventional methods render a flat image. SEM uses scattered electrons from the sample surface, either secondary or backscattered, thus rendering a tridimensional image. Electron microscopy uses electromagnets rather than lenses, and the researcher has much more control in the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the electron microscope one of the most useful instruments in research today.

The history of electron microscopy began with the development of electron optics. In 1926, Hans Bush showed that a magnetic coil can focus an electron beam in the same way that a glass lens can focus light. Nearly at the same time, the French physicist de Broglie introduced the concept of corpuscule waves (Bogner et al., 2007). In 1931, Ernest Ruska and Max Knoll at the Technical University in Berlin designed the transmission electron microscope (TEM) with a magnification of 16, with an electron beam instead of light, and electromagnets instead of lenses. In 1932, Knoll and Ruska tried to estimate the resolution limit of the electron microscope. Assuming the resolution limit formula of the light microscope was still valid for material waves, they replaced the light wavelength by the electron wavelength at an accelerating voltage of 75 kV. A theoretical limit of 0.22 nm resulted, a value experimentally reached only 40 years later (Bogner et al., 2007). In 1939

TABLE 1
Tabulation of analytical methods used in examination of atmospheric aerosols

References	Analytical methods	Subject of the investigation
Drewnick et al., 2008; Iijima et al., 2007	Aerodynamic particle sizer spectrometry (APS)	Measurement of aerodynamic diameters Analysis of particle size distribution
Drewnick et al., 2008	Aerodyne time-of-flight aerosol mass spectrometer (ToF-AMS)	Particle concentration and size distribution measurement
Lall et al., 2008	Aerosol particle mass analyzer (APM)	Classification by mass of aggregates with a given mobility diameter
Drewnick et al., 2008	Aerosol time-of-flight mass spectrometry (AToF-MS)	Particle concentration and size distribution measurement
Lu et al., 2008a; Bernabe et al., 2005; Karthikeyan and Balasubramanian, 2006; Gokhale and Patil, 2004; Rizzio et al., 2001; Ragosta et al., 2006; Thipse et al., 2002	Atomic absorption spectroscopy (AAS)	Total concentration measurement of metals
Bernabe et al., 2005	Atomic emission spectroscopy (AES)	Chemical composition of ∼60 detectable elements analysis
Gwaze et al., 2007	Atomic force microscopy (AFM)	Particle size determination
Lall et al., 2008; Drewnick et al., 2008; Fukuhara et al., 2008	Condensation particle counter (CPC)	Measurement of particle number and separated nanoparticle concentrations
Barone and Zhu, 2008; Lall et al., 2008; Fukuhara et al., 2008	Differential mobility analyzer (DMA)	Classification of aggregates according to their mobility diameter and separated nanoparticles
Tomasevic et al., 2005	Differential pulse anodic stripping voltammetry (DPASV)	Determination of trace metal contents
Osan et al., 2002	Electron probe microanalysis (EPMA)	Chemical analysis of selected volumes
Sarica et al., 2002; Macedo et al., 2010	Flame atomic absorption spectroscopy (FAAS)	Determination of metals (Al, Fe, Ca, Mg, Ba, Cr, Mn, Ni, Cu, Zn, Pb, Cd, V, and Sr)
Mihalopoulos et al., 2007; Leal-Granadillo et al., 2000; Parshintsev et al., 2010; Falkovich and Rudich, 2001; Ochsenkuhn-Petropoulou et al., 2003; Zhou and Ye, 1998; Mannino and Orecchio, 2008; Liang et al., 2006; Waterman et al., 2001; Welthagen et al., 2003	Gas chromatography (GC)	Organic compound analysis
Dixon and Baltzell, 2006; Oanh et al., 2005; Sotero and Arce, 2008; Piñeiro-Iglesias et al., 2004; Engling et al., 2006; Coscollà et al., 2008; Bellido-Martín et al., 2009; Moscoso-Pérez et al., 2008; Sánchez-Rodas et al., 2007	High-performance liquid chromatography (HPLC)	Analysis of organic compounds
Engling et al., 2006	High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD)	Studies of aerosol concentrations of anhydrosugars in smoke aerosol

(Continued on next page)

TABLE 1
Tabulation of analytical methods used in examination of atmospheric aerosols *(Continued)*

References	Analytical methods	Subject of the investigation
Suzuki, 2006; Kulkarni et al., 2007; Iijima et al., 2007; Moreno et al., 2007; Hutchinson et al., 2005; Buzica et al., 2006; Canepari et al., 2009; Smichowski et al., 2005; Boevski et al., 2000; Menzel et al., 2002; Lu et al., 2008b; Jayasekher, 2009; Zabalza et al., 2006; Yue et al., 2006	Inductively coupled plasma (ICP)	Some metals determination/bulk elemental content analysis
Fosco and Schmeling, 2007; Mouli et al., 2003; Ma et al., 2001; Chena et al., 2007; Borai et al., 2002; Bogo et al., 2003; Zabalza et al., 2006; Xu et al., 2010; Canepari et al., 2009	Ion chromatography (IC)	Ion analysis
Owega et al., 2002	Laser ablation/ionization mass spectrometry (LAMS)	Organic and inorganic component analysis
Leal-Granadillo et al., 2000; Lintelmann et al., 2010	Liquid chromatography (LC)	Analysis of polycyclic aromatic hydrocarbons (PAHs) Analysis of polycyclic aromatic nitrogen heterocycles (PANHs)
Wheeler et al., 2000	Microbalance	Filter weight analysis
Stefaniak et al., 2006; Potgieter-Vermaak and Van Grieken, 2006	Micro-Raman spectrometry (MRS)	Estimation of particle size and disordered character of the carbon
Drewnick et al., 2008; Petzolda and Schonlinner, 2004	Multi-angle absorption photometry (MAAP)	Mass concentration measurements of black carbon
Rizzio et al., 2001; Avino et al., 2008; Cao et al., 2002; Bem et al., 2003	Neutron activation analysis (NAA)	Determination of metals (Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb, Pb, S, F, Fe, Nb, Ne)
Bogo et al., 2003	Optical microscopy	Area and diameter observation of particles
Kandler et al., 2007; Drewnick et al., 2008	Optical particle counter (OPC)	Aerosol number size distribution measurement
Karthikeyan and Balasubramanian, 2006; Menzel et al., 2002; Ma et al., 2001; Bogo et al., 2003; Calzolai et al., 2008	Particle induced X-ray emission or proton induced X-ray emission (PIXE)	Determination of atoms with mass greater than sodium atom and smaller than uranium atom, mostly metals (Na, Mg, Si, S, Cl, Ca, Fe, Zn)
Wang et al., 2008	Particle size analysis (PSA)	Particle size and shape analysis
Bernabe et al., 2005	Polarized light microscopy	Mineralogical composition analysis
Frommea et al., 2008	Reflectometer	Measurement of filter absorbance
Barone and Zhu, 2008; Drewnick et al., 2008; Fukuhara et al., 2008	Scanning mobility particle sizer (SMPS)	Measurement of particle number-size distributions and particle diameter distributions
Konarski et al., 2006	Secondary ion mass spectrometry (SIMS)	Determination of tested particle morphology and structure
Bi et al., 2011	Single particle aerosol mass spectrometry (SPAMS)	Characterization of single particle size and chemical composition
Konarski et al., 2006	Spark source mass spectrometry (SSMS)	Bulk analysis
Ban-Weiss et al., 2008	Thermal optical analysis (TOA)	Carbon content measurement of quartz filter

(Continued on next page)

TABLE 1
Tabulation of analytical methods used in examination of atmospheric aerosols *(Continued)*

References	Analytical methods	Subject of the investigation
Engling et al., 2006; Sanchez de la Campa et al., 2009	Thermal-optical transmission (TOT)	Measurement for pyrolysis correction of organic carbon (OC) and elemental carbon (EC)
Fukuhara et al., 2008; Tomiyasu et al., 2004	Time-of-flight secondary ion mass spectrometry (TOF-SIMS)	Detailed composition analysis
Bernabe et al., 2005; Karthikeyan and Balasubramanian, 2006; Wang et al., 1997; Pramod, 2001	Ultraviolet-visible spectrophotometry (UV-VIS)	Ion (among others NH^{4+}, Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, NO^{3-}, SO_4^{2-}, Cl^{-}) and mineralogical composition determination
Testa and Mosello, 1996; Chabas and Lefevre, 2000; Canepari et al., 2009; Yu et al., 2008; Ebert et al., 2004; Schmeling et al., 1997; Yue et al., 2006; Niu et al., 2010; Calzolai et al., 2008; Perrino et al., 2009	X-ray fluorescence (XRF) Total reflection X-ray fluorescence (TXRF) Synchrotron radiation micro-beam X-ray fluorescence (micro-SXRF) Energy dispersive X-ray fluorescence (EDXRF)	Measuring elements from lithium to uranium and beyond
Bernabe et al., 2005; Rodriguez et al., 2009; Campos-Ramos et al., 2009; Wiinikka et al., 2006; Lun et al., 2003; Migliavacca et al., 2009; Queralt et al., 2001; Davis and Guo, 2000; Díaz-Hernández et al., 2011	X-ray powder diffraction (XRD)	Identification of crystalline phases

Ruska and Bodo von Borries developed a marketable electron microscope in the Siemens Laboratory for Electron Optics and Electron Microscopy, and in 1938 von Ardenne constructed a scanning transmission electron microscope (STEM) by adding scan coils to a transmission electron microscope. The first true SEM was described and developed in 1942 by Zworykin (working in the RCA Laboratories in the United States), who showed that secondary electrons provided topographic contrast by biasing the collector positively relative to the specimen (Bogner et al., 2007). The design was again reengineered by C. W. Oatley in 1948 while he was a professor at Cambridge University. In 1963, Pease and Nixon combined all of these improvements in one instrument: the SEM with three magnetic lenses and an Everhart-Thornley detector (ETD). This was the prototype for the first commercial SEM (Bogner et al., 2007), made in 1965 by the Cambridge Instrument Company in the U.K., who marketed it as the Stereoscan Mark I SEM (to be followed about six months later by JEOL in Japan). The SEM models we are using today are not very different from this first instrument. In the 1950s electron probe instruments were also built in France and used for X-ray microanalysis by Castaing and Guinier and for cathodoluminescence by Bernard and Davoine. A modified version of his technique, energy dispersive spectrometry (EDS), is nowadays usually added to the TEM or SEM.

The electron microscopy family includes:

- Transmission electron microscopy (TEM)
- Scanning transmission electron microscopy (S/TEM or STEM or (S)TEM)
- High-resolution transmission electron microscopy (HRTEM). This method has been widely used in recent decades to study the structure and properties of materials at the highest spatial resolution. HRTEM is identical to TEM imaging except that the magnifications used are high enough to easily see the lattice spacing of inorganic materials including ceramics, semiconductors, and metals. HRTEM can provide structural information at better than 0.2 nm spatial resolution. The major research field using high-resolution electron microscopy (HREM) is quantitative structure determination at atomic resolution.
- Environmental TEM (ETEM)
- Environmental high-resolution transmission electron microscopy (EHRTEM)
- Wet-environmental electron microscopy (Wet-ETEM) (Gai, 2001)
- Energy filtered TEM (EFTEM)
- Low-voltage transmission electron microscopy (LVTEM)
- Analytical transmission electron microscopy (AEM)
- Scanning electron microscopy (SEM)

- Computer-controlled SEM (CCSEM)
- Low-temperature scanning electron microscopy (LT-SEM)
- Field emission scanning electron microscopy (FE-SEM)
- High-resolution scanning electron microscopy (HRSEM)
- Low-voltage scanning electron microscopy (LVSEM). Operating at a few keV, this is an extremely powerful surface tool for both the structure and chemical analyses of nanocatalyst surfaces.
- Environmental SEM (ESEM)
- Reflection electron microscopy (REM), scanning REM (SREM)

Electron microscopy techniques have been used in numerous studies to characterize ambient particles over the past 40 years (Yakowitz et al., 1969; Dzubay and Mamane, 1967; Sartin and Murr, 1980), the first articles describing this field of interest appearing in the 1970s (Casuccio et al., 2004). Electron microscopy has proved to be an ideal tool for characterization of individual particles. TEM and SEM coupled with energy dispersive X-ray spectrometer characterization is well suited to provide such information on individual particles as morphology, elemental composition, mixing state, crystal structure, particle number, metals, crustal elements, and complex refractive index of atmospheric aerosol particles (Kandler et al., 2007; Casuccio et al., 2004). Using automation procedures, large numbers of individual particles in the size range from 100 nm up to 50 mm in diameter can be studied, with high statistical significance (Kandler et al., 2007). Electron microscopy can provide valuable information on the composition, sources, and atmospheric transformations as well as the number and volume-size distribution of atmospheric aerosols. These data are essential for the assessment of health effects of airborne particles, but cannot be obtained by mass measurement alone (Shi et al., 2003; Wilkinson et al., 2011).

TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy is a powerful tool for the characterization of materials (Figure 1). Some microstructural features are defined largely in terms of their TEM images. In this technique, the electrons are accelerated at high voltage (60–1,000 kV) to a velocity approaching the speed of light; they must therefore be considered as relativistic particles. The associated wavelength is five orders of magnitude smaller than the light wavelength (0.04–0.008 Å). This resolution enables material imaging and structure determination at the atomic level.

TEM can be employed to characterize individual particles. This microscopy offers increased resolution for identification of submicron particles and has the ability to provide information on molecular structure of crystalline particles using selected area electron diffraction (SAED) analysis in addition to obtaining elemental information using EDS techniques (Casuccio et al., 2004). Although a labor-intensive method, TEM has gained acceptance as a method of choice in the characterization of fine asbestos fibers and it can play a prominent role in the characterization of PM10 and PM2.5 (Casuccio et al., 2004).

SCANNING ELECTRON MICROSCOPY

The scanning electron microscope is one of the most versatile instruments available for the examination and analysis of microstructural characteristics of solid objects (Nemati, 1997). In SEM technique, a fine probe of electrons with energies typically up to 40 keV is focused on a specimen and scanned along a pattern of parallel lines (Díaz-Hernández et al., 2011). Scanning electron microscopy combined with energy dispersive X-ray spectrometry (SEM-EDS) is a nondestructive analytical method for surface elemental analysis, with a potential detection limit of 0.1–0.5 wt.% for most elements (Haley et al., 2006).

The primary reason for SEM's usefulness is the high resolution that can be obtained when bulk objects are examined. SEM allows a focused electron beam to be scanned across the sample while under vacuum. The interaction of the electron beam with the sample produces various effects that can be monitored with suitable detectors. Different signals are generated as a result of the impact of the incident electrons, which are collected to form an image or to analyze the sample surface (Bogner et al., 2007). The resulting signals, which include, among others, secondary and backscattered electrons along with characteristic X-rays, can be collected in synchronization with the position of the beam to provide highly detailed spatial and compositional information (Casuccio et al., 2004). The SEM has a large depth of field, which allows more of a specimen to be in focus at one time.

CHEMICAL MICROANALYSIS TECHNIQUES

Energy dispersive X-ray spectroscopy or spectrometry (EDS or EDX) is a chemical microanalysis technique acquired from small regions of the specimen illuminated with a focused electron beam (Tanaka et al., 2008). The elemental composition of a phase is determined using the characteristic X-ray spectrum of the examined specimen. It is a nondestructive analytical method for elemental analysis, with a potential detection limit of 0.1–0.5 wt.% for most elements (Haley et al., 2006). The EDS scintillation detector is capable of identifying elements with atomic numbers equal to or greater than five (boron), although quantification is very difficult for elements with atomic number below eight (oxygen) (Laigo et al., 2008). EDS can provide rapid qualitative, or with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1–2 microns.

Wavelength dispersive X-ray spectrometry (WDS) is a technique that surpasses EDS at high-energy resolution in its detection limits and its ability to detect light elements (Takana et al., 2008). WDS-equipped systems use diffracting crystals for X-ray discrimination and have X-ray resolutions of approximately 10 eV, therefore, chemical detection limits are 100 ppm or better (Cubukcu et al., 2008).

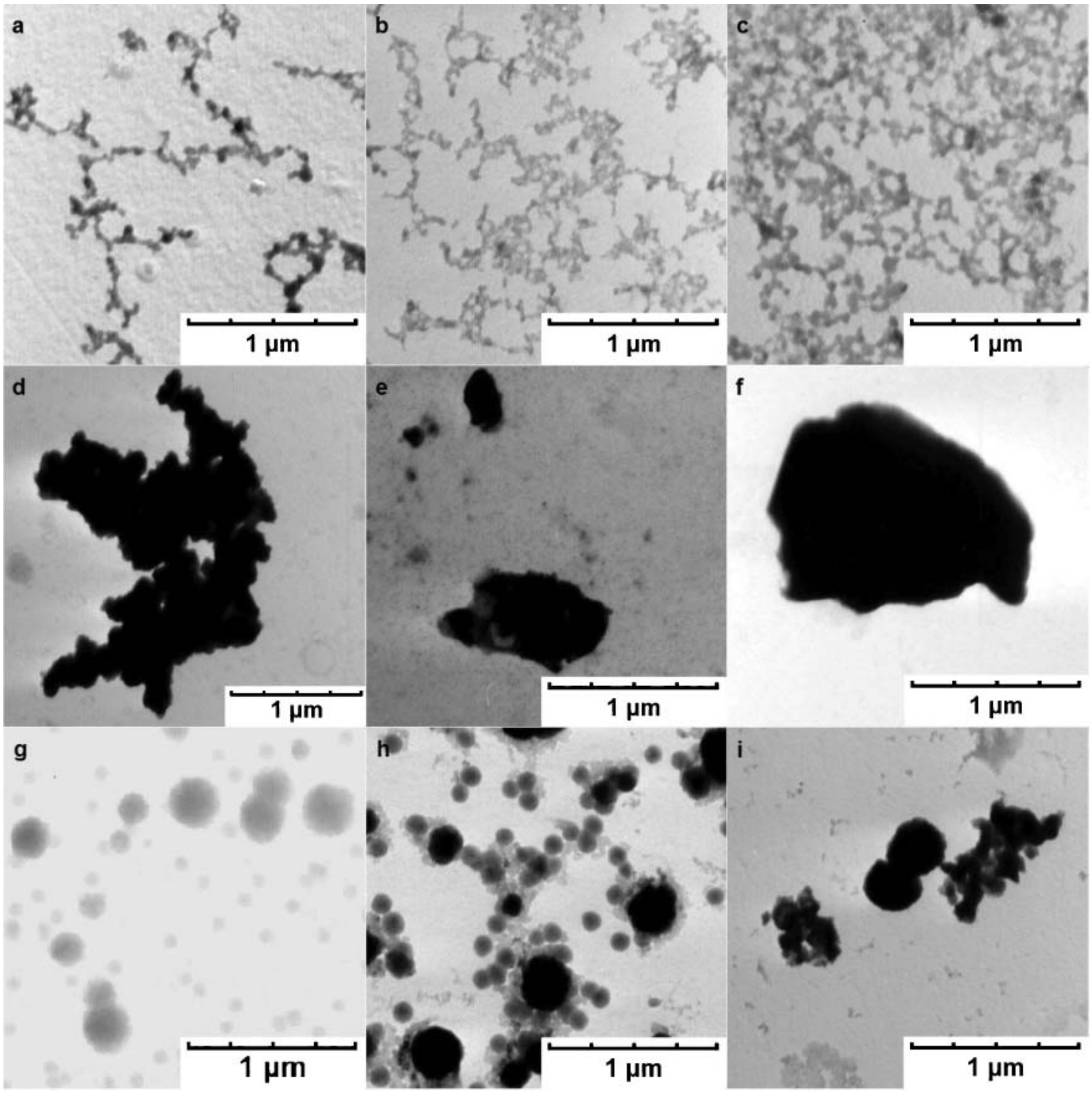

FIG. 1. TEM images: (a), (b), and (c) soot; (d), (e), and (f) irregularly shaped particles with a high carbon content; (g) and (h) circular particles of unburned fuel; (j) irregularly shaped particles (own data).

Electron backscatter diffraction (EBSD) is based on the acquisition of electron diffraction patterns from bulk specimens in the scanning electron microscope. A beam of highly accelerated electrons strikes a tilted specimen. The diffracted electrons form a set of paired large-angle cones corresponding to each diffracting plane. The regions of enhanced electron intensity between the cones produces the Kikuchi bands of the electron backscattered diffraction pattern (EBSP), which are then used to form an image on a fluorescent screen. Kikuchi bands can be interpreted in terms of crystallographic structure. More detailed discussion of the technique can be found, for example, in the review of Humphreys (Laigo et al., 2008).

Electron energy-loss spectrometry (EELS) is a technique where energy losses of the electrons are measured after high-energy electrons have traversed the specimen. It analyzes the energy lost by the incoming fast electrons when they travel through the sample. EELS is able to provide information about the electronic structure of the sample. This technique can also be used for chemical analysis and can provide quantitative information about the composition of the specimen.

X-ray microanalysis (XRMA) is a technique operated in scanning mode that can measure all major elements except for hydrogen. XRMA is based on the generation of characteristic X-rays in atoms of the specimen by the incident beam electrons. Quantitative analysis is carried out by comparing the relative X-ray intensity (defined as the ratio between characteristic and continuum X-rays) between the unknown and a standard with known composition. In order to minimize problems in the comparison of specimen and standard, the standard is made to resemble the specimen, e.g., mineral salts dissolved in a 20% gelatin matrix (Dragomir et al., 2004).

X-ray diffractometry (XRD) is a versatile, nondestructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD can be used to measure the average spacing between layers or rows of atoms, determine the orientation of a single crystal or grain, find the crystal structure of an unknown material, and measure the size, shape, and internal stress of small crystalline regions.

PARTICULATE MATTER SAMPLING

Sampling is a key stage for all electron microscopy analysis. This point determines the speed of the whole testing process and affects its result. In TEM analysis the sampling method has a particularly large importance. This kind of microscopy requires proceeding with a very thin (around 100 nm) disk-shaped sample with a diameter of 3 mm. The sample has to be flat and smooth, resistant to the electron beam, decontaminated, and nonmagnetic. The low thickness of the sample means that dust settled on filters cannot directly be observed in this technique (this is possible only in the case of thin polycarbonate filters).

For SEM techniques, sample thickness has no great importance, as in the case of TEM. Specimens do not have to be flat and smooth (SEM has greater image depth). Conventionally, SEM, unlike ESEM, requires using conductive samples. This is obtained by sample coating with a thin conductive layer (most often Au or Pt) (Figure 2). Due to the coating process the sample discharges, giving better quality images. However, the conductive layer may sometime falsify the results of elemental composition analysis of the tested sample.

For sampling, impactors are mainly used (Yu et al., 2008; Deboudt et al., 2008; Ortner et al., 1998; Mamani-Paco and Helble, 2007), often with separation into individual phases and with forced airflow. Particulate matter can also be collected onto various filters (Shi et al., 2003). These are mainly polycarbonate, Teflon, quartz fiber, glass fiber, and nylon filters (Casuccio et al., 2004). Each type of these filters has its own disadvantages. Teflon and polycarbonate (PC) filters are well suited for XRF analysis, but neither is suitable for carbon analysis, since a large quantity of carbon can be found in their composition. Anion/cations (e.g., ammonium, sulfate, and nitrate) can be determined using ion chromatography (IC) for samples collected on Teflon, nylon, PC, and quartz filters. The preferred substrate for SEM analysis is a PC filter. Optimal analysis of individual particles using electron microscopic techniques requires that particles be collected in a monolayer on a microscopically smooth substrate with a minimum of particles in contact (Casuccio et al., 2004). Filters made of fibers have one main disadvantage: particulates can settle in the depths of the filter and in the mesh of the fibers (Figure 3). This causes difficulties in particulate matter morphological analysis.

Less often, airborne PM can be collected on copper or nickel transmission electron microscope grids coated with a very thin formvar, carbon, or collodion film coated with an equally thin layer of evaporated carbon (Murr and Bang, 2003). This method seems to be very interesting since it minimizes difficult stages of sample preparation. Particulate matter samples are ready for TEM analysis, and SEM analysis requires only sample coating with a conductive layer. TEM's additional advantage is the low cost and analysis speed of samples collected directly onto microscopic grids. However, its main disadvantage is the possible appearance of peaks in the resulting spectrum from grid

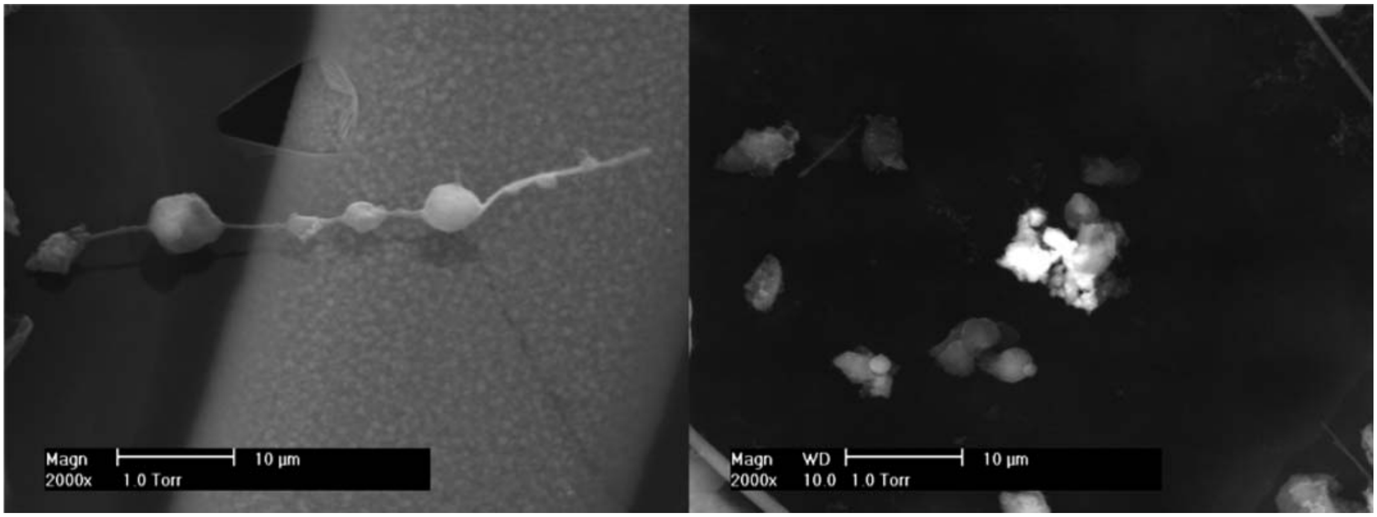

FIG. 2. Sample coated with thin layer of Au (left). A clear shadow is seen, appearing after sample coating. On the right is a noncoated sample (own data).

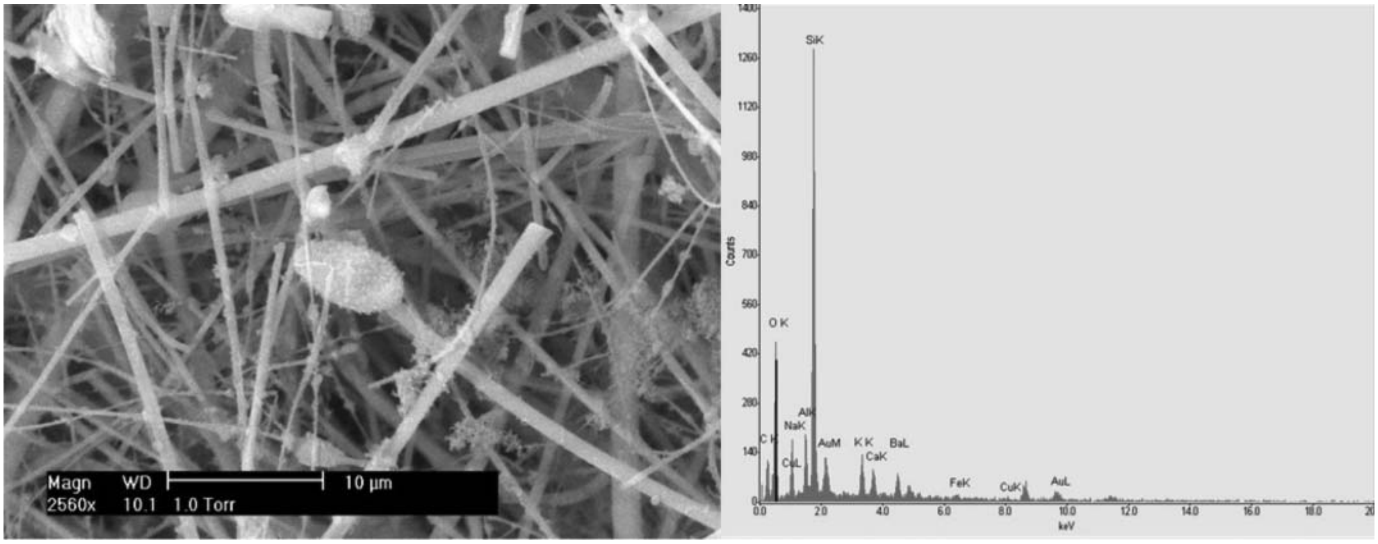

FIG. 3. Image of particulate matter settled on fiberglass filter and EDX Philips-FEI XL 30 ESEM with EDAX Sapphire spectrum. On the EDX spectrum a large peak can be seen indicating high content of Si in the tested sample. However, the detector signal probably originates from filter fibers composed of Si (own data).

construction material (Cu or Ni) during chemical composition analysis with the use of an EDX/EDS detector.

SIZE AND MORPHOLOGY OF PARTICLES

Size is the single most important determinant of the properties of particles; it has implications for formation, physical and chemical properties, transformation, transport, and removal of particles from the atmosphere (Vallius, 2005). Thus, most often size distribution and morphology of dust particles are tested with an electron microscope. These determinants among others are discussed by Kandler et al. (2007), Barone and Zhu (2008), Wheeler et al. (2000), Lall et al. (2008), Lu et al. (2008a), Thipse et al. (2002), Tomasevic et al. (2005), Bogo et al. (2003), Wang et al. (2008), Frommea et al. (2008), Chabas and Lefevre (2000), Ebert et al. (2004), Yue et al. (2006), Campos-Ramos et al. (2009), Kruegera et al. (2004), Geng et al. (2009), Kocbach et al. (2005), Kaegi (2004), Sitzmann et al. (1999), Xie et al. (2005), Liu et al. (2005), Kaegi and Holzer (2003), Choel et al. (2007), Martinez et al. (2008), Ormstad et al. (1997), Esbert et al. (2001), Yoon et al. (2011), and Sielicki et al. (2011a, b). Size distribution is important in establishing particle transport, deposition in the respiratory system, and light-scattering properties (McDonald and Biswas, 2004). Atmospheric particulate matter is commonly divided into ultrafine, fine, and coarse particle size fractions, which refer to particles with an aerodynamic diameter smaller than 0.1 μm (PM0.1) or 2.5 μm (PM2.5) or in the range of 2.5–10 μm (PM10), respectively (Vallius, 2005).

The importance of morphology as a potential contributor to toxicity can be related to the influence of morphology on both surface composition and particle transport properties (Mamani-Paco and Helble, 2007). Scanning and transmission electron microscopy studies have shown particles to have a variety of morphologies such as chain aggregates, solid irregulars, and more liquid/spherical shapes (Reid et al., 2005). Furthermore, morphology has an indirect but important effect on particle-size measurement: the sphere is the only object whose size can be defined by a single size parameter, its diameter (Pons et al., 1999).

Most atmospheric particles are not spherical and have a range of densities. Therefore, their diameters are often described by an "equivalent" diameter (i.e., Feret's diameter, Martin's diameter) (Wilson et al., 2002). Nonspherical particles have higher surface area than spherical particles of comparable aerodynamic diameter, thereby providing potentially more contact surface for lung-particle interaction. Irregular particles with high surface area also provide a condensation surface for by-products of combustion processes (Mamani-Paco and Helble, 2007). It is worth adding that there is still no standard size parameters that can help to compare the results coming from different laboratories. In our opinion it could be Feret's diameter.

In the measurement of number concentration, particle size segregation is often based on electrical mobility, whereas in the measurement of mass concentration the segregation is mostly based on aerodynamic diameter. The aerodynamic diameter is defined as the diameter of a unit density sphere having a terminal velocity equal to that of the given particle (Sillanpää, 2006). The aerodynamic diameter, important for particle transport, removal, collection, and respiratory tract deposition, is defined as the diameter of a spherical particle with a density of mg/cm^3 but with a settling velocity equal to that of the particle in question (Wilson et al., 2002). Unfortunately, calculation of aerodynamic diameter with the use of electron microscopy is not possible. This is a real problem, causing difficulties in comparison of results obtained by microscopy and other techniques. Therefore, for description of morphological parameters, most often length, area, perimeter, or a shape factor, i.e., a combination of size parameters, are used (Pons et al., 1999).

Improved understanding of PM morphology distributions is also an important factor in modeling the effect of fine particles on the absorption and scattering of radiation in the atmosphere, needed for accurate determination of the radiative forcing associated with fine atmospheric particles in calculating an energy balance to assess global climate change (Mamani-Paco and Helble, 2007). It is very important to select proper magnification for the size of particles tested. In accordance with Blanco et al. (2003), particles with diameter larger than 5 μm should be analyzed by using 500× magnification, those with diameter in the range 1–5 μm by 1,000× magnification, and those with diameter smaller than 1 μm by 3,500× magnification. For microscopic observation Deboudt et al. (2008) used constant magnification equal to 6,000×. Ormstad et al. (1997) used 5,000× magnification; particles between 0.5 and 2.5 pm had a size about equal to or less than 0.5 μm, therefore requiring higher magnification (approximately 25,000×) for counting in TEM.

For most observations, not very high magnifications are needed. In practice magnifications of 1,000× to 20,000× are generally set. These are rather small magnifications that any electron microscope can reach without any problem, but then, it is not possible to observe all structural details. Thus, to penetrate more deeply into the structure and morphology of particulate matter higher magnifications should be obtained.

For useful description of PM morphological parameters, image analysis software is used. It allows marking particle morphology (with quantitative information) in a quick and precise way (Pons et al., 1999). It should be mentioned that images taken by TEM seem to be more predisposed to morphological analysis than SEM images. This is due to better contrast of TEM images and therefore better precision in software measurement. Images from SEM are characterized by lower contrast, causing difficulties during image analysis (less advanced software is not able to classify particulate matter correctly).

Another disadvantage of SEM images is that on images made with the use of this technique many disturbing elements can be found during particulate morphological analysis (i.e., filter fibers). However, rapid progress in the image software area and constant development of calculation applications of computers, in conjunction with electron microscopy and image analysis, seems to point the right direction for further studies. Nowadays, automation possibilities of image analysis and high image taking speed with the use of electron microscopy controlled by computers give great capabilities to gather knowledge about PM morphology, and therefore information about its origin and harmfulness. Using automated procedures, large numbers of individual particles in the size range from 100 nm up to 50 mm in diameter can be studied, providing high statistical significance (Kandler et al., 2007).

Deboudt et al. (2008) estimated the minimum quantity of particulate matter for which the particle size has to be measured to get representative results. They stated that more than 500 particles have to be subjected to analysis and 1,000 particles per impaction stage is the optimal size.

Based on the images of particle surface shape gained by the SEM/EDS analysis, Wang et al. (2008), in a study of inhalable particles in Shijiazhuang City, China, identified six clusters of particulate morphology of PM10: irregular diamond, agglomerate, sphere, floccule, column or stick, and unknown, by quantitative order. Irregular-shaped grains of these particles have a coarse and holed surface, with average diameter of 8 μm. Some irregular diamonds have a rather smooth and flat surface. Agglomerate particles are fewer in number than the irregular diamond shapes but are a little larger in size. Flexuous fractal edge branches or crinkles present randomly outside the agglomerate grains' surface, forming the lump morphology. Sphere particles are generally smaller than all other particle types, with average diameter under 3 μm. There are three impressed surface patterns of the sphere particles in Shijiazhuang City: smooth, semi-coarse, and coarse. For floccules analyzed by amplified observation, it was found that these grains are made up of tiny spherical particles normally less than 1 μm. It seems that these floccule particles are structured loosely and have alterable size, but in this research, most floccules-shaped grains possess an apparent size of about 10 μm. Column or stick particles, shaped long and elliptically, usually bear some physiological texture externally. Some deformed or nondescript particles account for a minority of the samples.

Based on the morphological features, and studies taken from articles of other authors, Wang et al. (2008) considered that the irregular diamond particles are assuredly derived from soil and surface geological deposits as the product of mechanical abrasion. The agglomerate and sphere particles are from the combustion of coal, while the floccule particles are from the discharge of vehicles, and the column- or stick-shaped particles are from bioactivities, but the numerical ratio of the above particles cannot directly indicate the source apportionment (Wang et al., 2008). The particle surface characteristics were also analyzed.

In addition, Campos-Ramos et al. (2009), based on a sample composition obtained with the use of EDX and images taken from SEM, divided the particles into categories: porous texture, ultrafine agglomerate, irregular, spheroidal, edges defined, spheroidal, crystal tabular, and agglomerates.

McDonald and Biswas (2004) observed in their study a small variation in fractal dimension, and larger variations in the aerosol shape distribution. As such, it is proposed that the shape distribution is also a valuable a tool for describing an aerosol. Detailed studies are under way in the greater Cincinnati air shed to evaluate trends in morphology (fractal dimension and shape distribution) as a function of the distance from a highway, to help determine the impact that diesel trucks play on ambient aerosol morphology (McDonald and Biswas, 2004).

Blaha et al. (2008) focused on investigation of bulk fly ash and provided an overview of the most prominent and frequent particle sizes and structures. They stated that nearly all particles are of spherical shape. Only a small amount of "loosely attached" agglomerates were observed.

Esbert et al. (2001) analyzed particles from images taken by SEM. These particles were collected by the sampler and on surfaces that could be individually discriminated. One characteristic determined was to separate the particles of each fraction and calculate their geometric areas by means of Featurescan.

Lu et al. (2008b) with the use of ESEM tested samples of PM2.5 from Shanghai. They divided tested particles into soot aggregates, coal fly ash, bio-particles, minerals, and unidentified particles. According to the shape and composition of particles identified by EDX, they could be generally divided into two groups, regular-shape particles and irregular particles. Regular-shape particles include soot aggregates, coal fly ash, biological particles, sulfate mineral particles, and pin-shaped mineral particles. Irregular shape particles are irregular mineral particles and unknown particles.

Finally, Mamani-Paco and Helble (2007) analyzed TEM grid samples with TEM microscopy followed by image analysis of digital TEM images. These digital images were analyzed by a software program that accomplished the perimeter identification (thresholding) of particle images and the calculation of corresponding perimeter fractal dimension for each particle border. The fractal dimensions of at least 40 particles corresponding to specific cutoff diameters were then saved and used to develop histograms of fractal dimension as a function of particle aerodynamic diameter.

PARTICULATE MATTER CHEMICAL COMPOSITION

The chemical composition of particulate matter is essential information for assessment of its sources and health effects. Thanks to knowledge about its composition one gets a wider look at the potential harmful effect of PM. Electron microscopy in conjunction with detectors is the right equipment to provide us with information about elemental composition of each PM particle. Many articles on analysis of PM composition with the use of electron microscopy have already appeared (Lu et al., 2008a; Thipse et al., 2002; Tomasevic et al., 2005; Bogo et al., 2003; Stefaniak et al., 2006; Wang et al., 2008; Chabas and Lefevre, 2000; Ebert et al., 2004; Yue et al., 2006; Campos-Ramos et al., 2009; Kruegera et al., 2004; Geng et al., 2009; Kocbach et al., 2005; Kaegi, 2004; Sitzmann et al., 1999; Xie et al., 2005; Liu et al., 2005; Kaegi and Holzer, 2003; Choel et al., 2007; Martinez et al., 2008; Ormstad et al., 1997; Esbert et al., 2001; Williams et al., 2008; Magiera et al., 2011; Agrawal et al., 2011; Sawyer et al., 2011; Pipal et al., 2011; Cambra-López et al., 2011; Saragnese et al., 2011; Sielicki et al., 2011a, b). From elementary analysis, information about the element content in each sample can be obtained. Unfortunately, this does not inform us which compound it is, and it is a huge disadvantage, if we wish to get data about organic compounds that may compose particulate matter (i.e., these compounds may be adsorbed onto the PM surface during the combustion process).

The EDX spectrometer is the instrument used most often. It seems that its popularity results from the fact that this detector is installed the most frequently in TEM and SEM microscopes. The great advantage of these detectors is their easy handling. It is enough to point to the place for signal collection by the detector and wait from 30 s to 2 min. After this short time a spectrum with peaks showing element content in the sample and their quantity will appear. Usually, the software automatically describes all peaks, and therefore spectrum interpretation seems to be not complicated. However, this kind of detector has disadvantages. EDX spectrometers are quite expensive and not all microscopes are equipped with them. Some of these spectrometers need to be cooled with liquid nitrogen, which makes the handling more complicated. EDX's main characteristic (not necessarily a disadvantage) is that the signal is mostly collected under the sample surface from a rather large volume (Figure 4). This feature maybe a weakness of this equipment in the case of testing very small particles or particles with very low density (and this is how atmospheric PM is consisted). When the particulate matter is smaller or thinner than the volume the signal is collected from, the signal could be collected from the background or ambient filter. Therefore, during analysis of particulate matter settled onto a filter made of fibers, the resulting detected signal will contain information also taken from the fibers (Figure 3). Moreover, if the PM surface is not flat (which happens almost always) or is not homogeneous at the place of analysis, the result may be falsified. In spite of its disadvantages, this type of spectrometer is applicable in chemical analysis of single PM.

In each study of TEM and SEM analysis of PM, the authors use their own particle division. One of the most detailed classifications was applied by Xie et al. (2005). They divided PM particles onto 17 particle types: silicomanganese slag, soil and fly ash, coal burning, silicomanganese, quartz, syngenite, S-bearing iron, calcium-rich, gypsum, sphalerite, dolomite, iron, alloy, lead sulfate, zinc-rich, sulfur-rich, and aluminum manufacturing dust. Ebert et al. (2004), based on composition obtained from spectrometer EDX and particle morphology, divided PM into: alumosilicates, silica, sea salt (including aged sea salt), calcium sulfates, ammonium sulfates, metal oxides/hydroxides, soot, biological particles, carbon/sulfate mixed particles, and the remainder carbon-rich particles. Geng et al. (2009) differentiated particulate matter was into primary soil-derived particles (AlSi-containing, SiO_2-containing, $CaCO_3$, $CaSO_4$ (gypsum)), secondary soil-derived particles, marine particles (genuine sea salts, reacted sea salts, reacted sea salts, and mixture), carbon-rich particles, organic particles, droplets rich in C, N, O, and S, K-containing particles, Fe-containing particles, and finally fly ash.

A schematic diagram of PM classification given by EDX spectrum was introduced by Lorenzo et al. (2006). They proposed a schema of PM classification according to element content in a given particle. The main division criterion for PM was the maximum content of a given element. Therefore, depending on which element constitutes the main component of a PM particle, we can assign particles into one of six groups: Fe-rich,

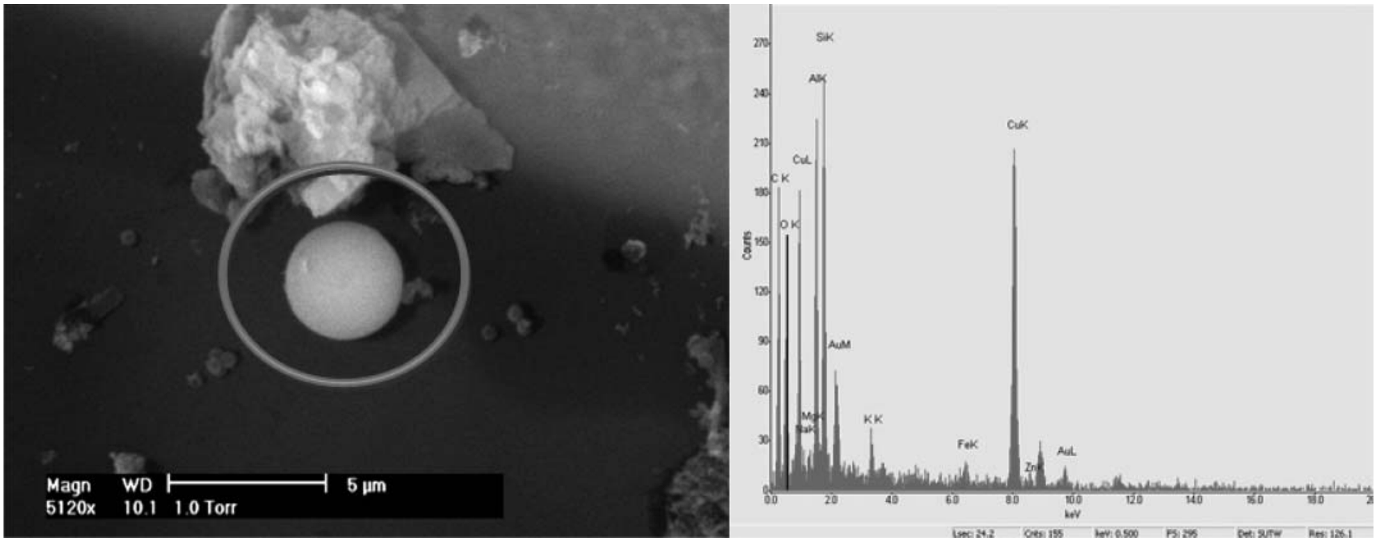

FIG. 4. Standard SEM image of PM and its EDX spectrum (own data).

Si-rich, Al-rich, S-rich, Ca-rich, and others. Particles with high Fe content are assigned to the iron particle class (Fe_2O_3). Si-rich particles are divided additionally into particles with and without Al content. Thus, depending on Al quantity, PM are classified into either aluminium particle class or silicon particle class. In accordance with Lorenzo et al. (2006), if a particle contains mainly Si and Al, and additionally Ca, the PM is constituted by $CaAl_2Si_2O_8$. However, if a particle does not contain Ca, the PM is constituted by $(Na,K)AlSi_3O_8$. Al-rich particles are assigned to the aluminium particle class (Al_2O_3). Particles with high content of S, depending on additional Ca amount, are divided into two groups: calcium particle class ($CaSO_4$) or sulfur particle class (various). If a PM particle contains mainly Ca, it belongs to the calcium particle class. Depending on the presence of S, it can be constituted by CaSO4 or $CaCO_3$ compounds. If a particle does not fit into any of these groups, the authors suggest to assign it to an "others" group. Precise PM classification schema can be found in Lorenzo et al. (2006). The proposed classification seems to be quite simple and fast in use. However, there is the lack of a particle class for those with high C content (i.e., soot) and sea salt particles.

A very simple particulate matter division was proposed by Kaegi and Holzer (2003), who also classified PM according to element content. However, they took into account only elements that constitute the majority of the particulate makeup. Sulfur was an exception, because the authors made a special formula helpful in particle assignment into the proper class. Therefore, PM can be easily divided into "silicate" particles, "iron-rich" particles, and so on.

A similar classification was presented by Sitzmann et al. (1999). The authors, with the use of an EDX detector, discovered the elements C, N, F, Cu, Na, Mg, Si, S, Cl, Cd, K, Sn, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Pb, Al, Zn, Pt, and Mo in atmospheric particulate matter. They divided the particles into C-rich, Fe-rich, Fe/Si-rich, Si-rich, Ca-rich, K-rich, S-rich, and unclassified.

Li et al. (2011), based on morphology and elemental compositions, classified particles into five groups: Si-rich particles, Ca-rich particles, Fe-rich particles, K-rich particles, and S-rich particles. Most of the particles were irregularly shaped.

Except for testing of PM morphology and composition, research has been focused on mineralogical phase composition and identification (Kandler et al., 2007; Bernabe et al., 2005) and elemental mapping (Liu et al., 2005); identifying the physical structure (Wheeler et al., 2000; Kaegi and Holzer, 2003); mixing state analysis (Geng et al., 2009); accuracy of the separation (Fukuhara et al., 2008); water uptake (Semeniuk et al., 2007); and mass balance (Williams et al., 2008).

ADVANTAGES AND DISADVANTAGES OF ELECTRON MICROSCOPY AIR PARTICLE ANALYSIS

Both transmission and scanning microscopes work under vacuum. A vacuum system makes the electron beam stable and disables interaction of gases with the electron gun, prolonging its life. If not operating under vacuum, the electron bean would cause gas ionization and accidental discharges. Moreover, the beam path through the electron lenses would be disturbed. However, despite its advantages, the vacuum in an electron microscope may cause destruction of particulate matter with high water content, especially in the case of biological dust particles (Figure 5). High vacuum may also cause the change of particles chemical composition.

Methods of particle morphology testing with the use of TEM and SEM do exist and are applied more frequently. However, the use of electron microcopy for atmospheric PM analysis is sometimes problematic taking into account the whole procedure from sampling stage up to particle size final analysis (different characterizing parameters are used) (Geng et al., 2009;

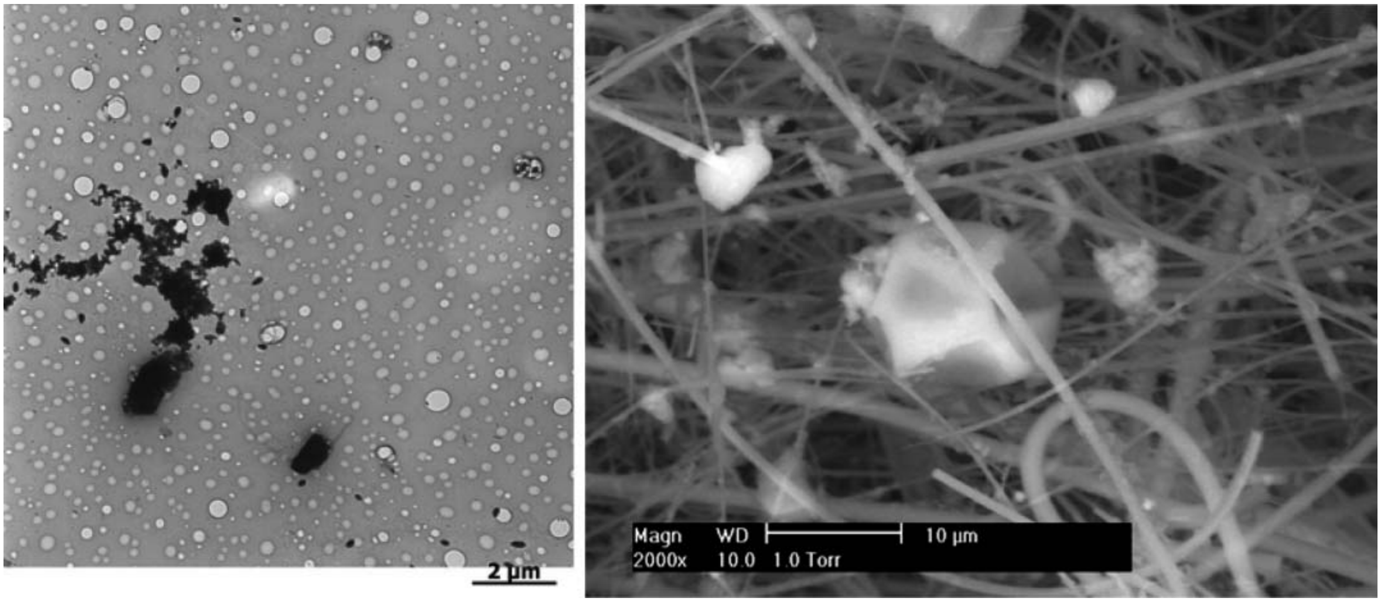

FIG. 5. Standard TEM image (left) and image of a particle that collapsed due to the vacuum system in the electron microscope (right) (own data).

Pons et al., 1999), as there is no standard procedure for all laboratories. Specimen preparation is also time consuming, needs to be precise, and requires proper skills and experience. It sometimes involves use of complex tools. The prepared specimen cannot undergo contamination, abrasion, or breakage of support film, in the case of TEM samples.

Sometimes samples may deform and distort the material tested, resulting in a false image in the case of improper preparation. Scanning electron microscopes are slower than transmission microscopes because the sample surface is scanned point by point, while in the TEM electrons passing through the sample are registered. Moreover, the SEM scans minor areas, with the edge length 1–10 μm. This limitation means that observing interesting details in a greater area or analysis of bigger particulates is impossible. However, the image obtained by SEM has the value of showing the sample surface, while on TEM images only particle shapes can be seen. Also, the EDX detector has some limits. It is hard to analyze lighter elements like sodium, nitrogen, and carbon with its usage. This causes difficulties in analysis of carbonaceous particles and soot. The EDX detector has one more disadvantage, which can be seen in the elemental analysis of ultrafine particles. The detector collects signals from a larger volume than particle size. This signal reaches the detector from the depth of around 1–4 μm (depending on detector setting and possibilities). This means that most of the analyzed spectrum is the spectrum of background elemental composition, especially from the surface where the PM particle is settled.

Another important task is to create uniform analytical procedures for particulate matter analysis with the use of electron microscopy. Nowadays, it seems easier to separate procedures for TEM and SEM. Both methods differ so much that creation of one procedure for these two kinds of electron microscopy is useless. If we consider current methods of atmospheric particles analysis by TEM, all are very complicated.

One promising technique in PM analysis is collection of particulate matter directly onto a microscopic grid covered with supporting film. Thus, the preparation stage can be omitted. Moreover, the time of particulate matter collection onto the microscopic grid should be defined (i.e., from 12 to 24 h for gravimetrical dust sampling or a few seconds for forced flow of atmospheric air sampling). Observing a sample in only one set magnification (i.e., 10,000×) can also reduce time of analysis and will give reproducible results with the use of different TEM setups in various laboratories.

The magnification should be suitably selected to make analysis of the largest spectrum of particle sizes possible. There might be a need to select two or three magnifications to analyze particles with diameter higher than 10 μm and lower than 0.01 μm (i.e., 1,000×, 10,000×, 100,000×).

In an improved method a minimum particle quantity for classification of a single sample should be determined. The sample should be big enough to obtain the volume for size distribution of single particles. The minimum quantity for particle size distribution is 100 particles and the optimal one around 1,000 particles. Moreover, the quantity of PM particles analyzed by an EDS detector should also be defined. The particle amount should be small enough in order to not lengthen the time of analysis, and at the same time big enough to provide qualitative information about dust content. Unfortunately, not all microscopes are equipped with EDX detectors or any other detectors of composition; therefore, elementary analysis of particles would not be possible on any microscope. The whole procedure should be short enough to obtain rather quick information about dust content and particle size distribution. The speed of this process is extremely important during monitoring of environmental contamination.

Moreover, the sampling process with the use of SEM should be uniform. Dust collected on filters can be analyzed, and sampled in other ways. One promising method seems to be particulate matter analysis on polycarbonate (PC) filters. This method is quite easy, and PM settled on the filter surface are not covered by filter fibers. A drawback is filter composition; PC filters are mainly made of C, therefore C content analysis in the dust may be impossible to accomplish. Still, it does not matter which sampling method is applied, since most microscopes require samples covered with a conductive layer. Most samples will be covered with a Au or Pt layer, rather expensive materials. On an EDX spectrum peaks from the conductive layer will appear and this is one disadvantage of using covered samples. These peaks may complicate analysis of other elements. Some types of SEM microscope do not require a sample conductive layer, thus the stage of sample covering can be omitted. Moreover, particle size can be easily measured with the use of the SEM. Also, constant magnification values can be set. which will facilitate and speed up the analysis process. All magnifications could be easily set on the same level as magnifications applied for TEM. The quantity of classified particles maybe the same as in the case of TEM (around 1,000×). The same elemental content with the use of detectors may be determined by both TEM and SEM.

As can be seen, new methods for dust analysis with the use of TEM and SEM might be similar and one method could be worked out. Particulate matter sampled onto microscopic grids can be analyzed both on TEM and SEM.

ESEM equipped with an EDX detector can be treated as an optimal system for PM analysis. With its use we get information about single-particle surface morphology, size distribution, shape, and elemental composition. It allows the presence of a gaseous or aqueous vapor environment in the specimen chamber, eliminating sample preparation. It facilitates and speeds up analysis considerably (Blanco et al., 2003). In considering TEM application, the HRTEM technique is promising. The great magnification of this microscope allows observing even the tiniest details of particulate structure. Recognition of the dust structure with the use of high magnification may explain how particulate matter was created and the structure of these particles.

For particle size distribution, size calculation is an important task. Usually, when particle diameter is determined the aerodynamic diameter is given. Unfortunately, calculation of aerodynamic diameter is rather impossible to do based on microscopic images. Therefore, it is worth setting another diameter for particles analyzed with the use of electron microscopy. It can be the Feret or Martin diameter, or else the length and width of the particle. Some authors use only the term “diameter,” which is misleading during result interpretation. The simplest and the fastest way to determine the size and morphological parameters is to use image analysis software, i.e., MultiScan, SigmaScan Pro, or ImageJ, or any software equipped with the microscopes. Unfortunately, each software differs, which influences the size results obtained. Software available today gives great opportunities for morphological parameter determination, and it is worth using them for image analysis.

SUMMARY AND CONCLUSIONS

Knowing that size of particulate matter occurring in the environment is getting smaller, current methods determining PM concentration seem to be insufficiently precise. Therefore, a new method for identification of ultrafine particles needs to be worked out. In the future, the new methods TEM and SEM can be introduced as the standard method for the tiniest atmospheric particles measurement. Creation and introduction of powerful aerosol testing methods are inevitable, due to more restrictive regulations regarding air cleanness and the necessity of environmental monitoring precision.

Introduction of electro-microscopic observations of particulate matter PM and PM2.5 analysis (collected on filters in monitoring stations), even at the present stage, provides quantitative and qualitative information as well as information about PM elementary composition.

Thus far, research on electron microscopy applications in atmospheric particulate matter analysis confirms its usefulness and great future opportunities. It was shown that detailed analysis of a single particle is possible, as well as determination of parameter range and PM properties, all during one analytical procedure. Constant progress in the field of investigation techniques and possibilities of method simplification predict process improvement. Especially, progress in the field of digital techniques gives new possibilities for method simplification, automation, objectivity, and good resistance.

Very promising is research with the use of electron microscopy combined with other analytical methods and techniques. Other research methods allow verifying results obtained by electron microscopy and, in addition, have benefits from the ability to study particle composition or size (depending on which methods are used). A highly interesting field of study is to utilize meteorological information, which is helpful in PM source estimation (Ebert et al., 2004; Geng et al., 2009). All studies focused on the dust emitted from specified sources (Chandler et al., 2007; Müller et al., 2005) or biomass combustion (Semeniuk et al., 2007) are also instructive, allowing the classification of each type of dust (with the content and morphology determined).

It seems that highly developed electron microscopy does not have many disadvantages, and in fact application of electron microscopy is a huge step ahead in PM structure analysis.

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