Environmental Pollution 159 (2011) 311–318

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

New tabletop SEM-EDS-based approach for cost-efficient monitoring of airborne particulate matter

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Demonstration of method for novel scanning electron microscopy in environmental monitoring of chemical constituents of particulate airborne impurities.

ARTICLE INFO

Article history:
Received 24 April 2010
Received in revised form
30 July 2010
Accepted 18 August 2010

Keywords:
Monitoring
Particulate matter
PM
Scanning electron microscopy
Element analysis

ABSTRACT

Recent developments in scanning electron microscopy (SEM) have produced tabletop instruments capable of reasonable imaging resolution at less cost compared to conventional equipment. Combining the SEM with energy dispersive spectroscopy (EDS) allows the possibility of elemental analysis through detection of X-rays emitted from interaction between individual particles and the SEM electron beam, revealing their atomic composition. It's well known that exposure to inhalable particulate matter (PM) poses health risks and routine monitoring of the chemical content of these has been realized. Exposure information is of a general character but by combining the chemical build-up of monitored particles and knowledge of their inherent health effects will allow better risk assessment. An analysis technique using a tabletop SEM with EDS is demonstrated on particles collected onto nucleopore filters from urban, industrial and rural areas. Detailed characterization of the instruments analysis capabilities as applied to PM are described.

1. Introduction

People spending time in- or outdoors are all subject to inhalable Particulate Matter (PM) in different forms such as an ever present ambient mineral suspension, vehicular and/or industrial activity or dust. Concentrations of PM vary on a local scale but many studies have linked inhaled PM to negative health effects (Lebowitz, 1996; Künzli et al., 2000). Considerable evidence, as shown by The World Health Organization (WHO, 2000, 2006), indicate that three classes of PM (PM10, −2.5 and −0.1, number corresponds to a μm-size cut-off limit) can have different sources and subsequently differing health impact due to deposition in different areas of the lungs (moderated by size mode) when inhaled where the inherent toxicity of the PM comes into effect. Reports by (Donaldson et al., 2001; Sioutas et al., 2005; Delfino et al., 2005) indicate that PM0.1 are retained in the lungs but are of a small enough size to enter the blood stream directly through the gas exchange mechanism in the lungs and (Nemmar et al., 2002) have shown that particle solubility issues may play a significant role in the health impact of this size mode of particles.

The European Union and the United States have both implemented legislation for permitted levels of PM in inhabited areas adopted from recommendations from (WHO, 2000; Pope et al., 2009). See (Brunekreef and Holgate, 2002) for an exhaustive discussion on the subject. According to (Bernstein et al., 2004) outdoor PM emissions are derived mainly from traffic-related and combustible sources and are mixed together with ambient suspended mineral materials whereas indoor sources vary greatly. PM-levels are often reported in terms of grams per cubic-meter ($\mu g/m^3$) determined either gravimetrically or computed from a mean particle abundance measurement using a mean density of background materials. This information is of a very general character and does not really differentiate PM on a chemical level, where inherent toxicities can vary greatly for comparable amounts of different materials. As such the health impact should be considered different for different inhaled materials (Soto et al., 2008; De Viscaya-Ruiz et al., 2006; Karlsson et al., 2009). In a general view any background material could be considered uniformly distributed and any anthropogenic sources, subject to meteorological dispersion, as heterogeneous and locally variable. Due to revisions to several countries PM emission policies and rising environmental awareness the need to monitor and characterize PM is growing.

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doi:10.1016/j.envpol.2010.08.024

This characterization should not be limited only to size, shape and a general assumption of constituents but should also provide data on chemical species and inherent toxicity derived from toxicological studies.

Characterization of PM on a routine basis is possible. The most common methods are off-line where samples are collected in the field and then analyzed in the laboratory utilizing microanalysis techniques such as Scanning electron microscopy (SEM) and X-ray fluorescence (XRF) (Morata et al., 2008; Viksna et al., 2004; Perrino et al., 2008; Godoi et al., 2008; Bennet et al., 2005; Miranda and Tomaz, 2008; Pérez et al., 2008). Chemical information can thus be acquired from individual particles using Energy Dispersive Spectroscopy (EDS) and a certain degree of automation is possible for larger sampling sizes. The main disadvantages of this type of analysis is that it is limited by particle size, where routine measurements of particles that are significantly smaller than 1 μm can be fraught with difficulty and result in poor analysis results. Running costs of instruments and expert personnel for these applications could be added drawbacks hindering routine use. For smaller size modes of particles (PM $<$ 1) other more sensitive methods such as Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Gas-Chromatography Mass Spectroscopy (GC–MS) can be used (Kleeman et al., 2009). These instrumentation methods are also well suited for analysis of the organic elements, which SEM and XRF can analyze to some extent, and also some functional groups or molecules can also be distinguished providing some clues as to possible toxicological effects from analyzed particles. Often they are less well suited for analysis of larger particles as some material break-up or desorption from the particle is needed for analysis and this invariably takes place on the surface of the particle and thus a proper representation of the particle as a whole remains uncertain, although it could be argued that any toxicological effects from particles arise from surface transactions making the surface the valid part to analyze it is also important not to disregard solubility of chemical species from particles. Prather et al. (1994) showed that on-line analysis of aerosols is possible using Aerosol Time-of-Flight Mass Spectrometry (ATOF-MS) in that an aerosol is introduced into the instrument and real-time analysis of the aerosol is made in a similar manner as in ICP- and GC–MS. ATOF-MS is a powerful tool for analysis due to fast 'fingerprinting' of known chemical species and classification of typical particle emission types that can be cross-referenced in a database of known species (Sodeman et al., 2005). Again it is well suited for analysis of sub-micrometer particles, if not the premier method for this application and outperforms SEM and XRF in this regard.

Recent developments in commercially available tabletop Electron Microscope equipment have led to new SEM development to bridge the gap between optical microscopes and conventional SEMs. Tabletop SEMs are both cheaper and easier to use than more conventional instruments and maintain magnification possibilities up to ×20 000 and resolution possibilities that are close in order to more conventional apparatus. These kinds of instruments have the inaccessibility of altering running settings, such as accelerating voltage, emission current or degree of vacuum when imaging a sample. Conversely this apparent disadvantage can be made an advantage as the factory settings of this kind of instrument are well suited for viewing a multitude of samples with very little to no pretreatment of samples, making it easy to use for an untrained professional. Tabletop SEMs are underperforming compared to the more technologically advanced analysis variants described above but hold their own when comparing full instrumentation cost, which is in the region of $100,000 US, and their ease of use. They are thus mainly suited for routine work. Tabletop SEMs can be fitted with EDS-detectors giving the user the option of scanning an area or a spot for elemental composition. This has been utilized in the current study. Particles caught on a substrate can in this way be analyzed for atomic content by focusing the electron beam in the instrument on an isolated particle and detecting X-ray emissions in the process. Spot sizes vary but generally they are approximately 1 μm^2 for this type of instrument. New piezoelectrically-cooled Silicon Drift Detectors (SDD) for EDS can be brought down in temperature to approximately −40 °C and alleviate the use of liquid nitrogen as cooling agent substantially reducing running costs.

In this study a possible methodology of particle microanalysis using a tabletop SEM was tested. Specifically a *Hitachi TM-1000* SEM with EDS was used. These come fitted with a Backscatter electron detector that not only gives visual imaging magnification up to ×10 000 but the backscatter also distinguishes electron density in the sample showing denser, i.e. heavier elements as brighter and the lighter elements as darker. The instrument runs under variable pressure mode (VP) which means in essence that excess charge build-up on the sample surface is led away by the trace amounts of gas in the sample chamber thus negating the requirement of coating of most samples. The EDS is capable of qualitatively detecting elements of atomic number 11 (sodium, Na) and higher in individual samples down to 300 nm in size, in some cases even smaller samples can be analyzed. Detection of elements lighter than Na is currently not possible using the standard instrumentation and thus the characterization of elements in the organic mode is beyond the scope of this analysis method. Comparative quantification of elements in particles is possible with computer software calculations on collected spectra presenting a possibility of tracing

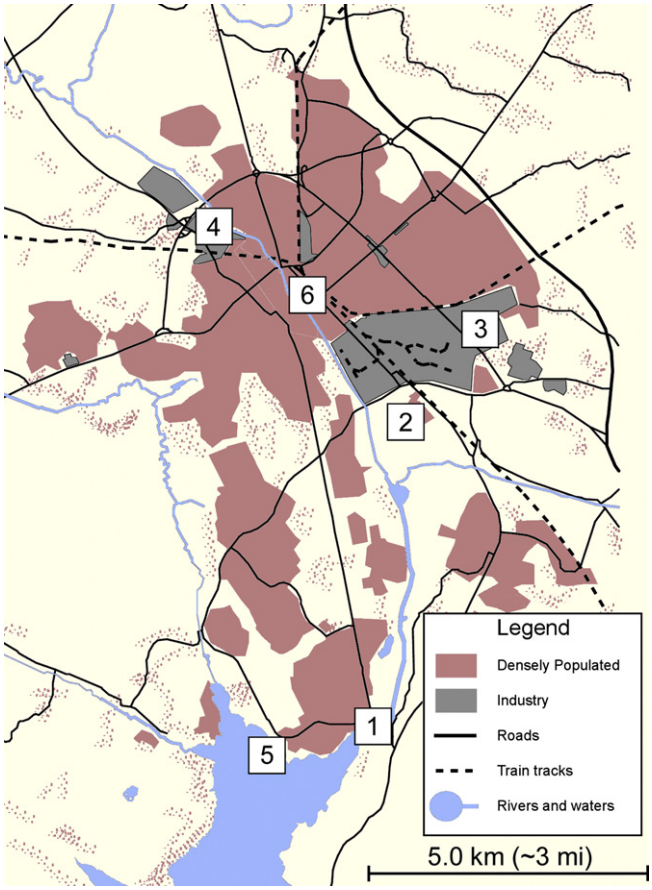

Fig. 1. Schematic representation of the city of Uppsala. Numbers denote sampling locations. 1) Flottsund [rural], 2) Kungsängen [rural], 3) Boländerna [Industrial], 4) Librobäck [Industrial], 5 Skarholmen [rural] and 6) Kungsgatan, Drottninggatan and Stora Torget [Central City].