Atmospheric Environment 75 (2013) 1–5

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

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

Short communication

Measurement of the specific surface area and particle size distribution of atmospheric aerosol reference materials

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ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form
8 April 2013
Accepted 12 April 2013

Keywords:
BET specific surface area
Chemical composition
EC/OC
Particle size distribution
$PM_{2.5}$
Standard reference materials

ABSTRACT

The investigation of the surface area of atmospheric aerosols is important as it provides a metric for their adverse health effects; however, few previous studies have considered this parameter. This study investigated the BET specific surface areas of aerosols, as well as the particle size distributions and chemical compositions of the three commercially available atmospheric aerosol reference materials; namely SRM1649a, CRM#28 and CRM#8. SRM1649a and CRM#28 consist mainly of coarse particles, while CRM#8 consists mainly of fine (or ultrafine) particles. The specific surface areas of the reference materials were; SRM1649a: $2.0 \pm 0.2\ m^2\ g^{-1}$, CRM#28: $2.0 \pm 0.2\ m^2\ g^{-1}$ and CRM#8: $35.7 \pm 5.3\ m^2\ g^{-1}$. CRM#8 had a higher value for the specific surface area. The specific surface area for CRM#8 was likely to be associated with the characteristics of diesel particulate matters. When the estimation of specific surface area of aerosol particles is based on the assumption that all particles are spherical and not aggregates/agglomerates, using particle number and mass distribution, the estimated value is likely to be significantly lower than the actual value, in particular, for fine or ultrafine particles. The actual specific surface area of atmospheric aerosols should be measured to avoid the underestimation of their adverse health effects.

1. Introduction

Aerosol particles are potentially harmful to humans; therefore, atmospheric aerosol exposure represents a serious concern for human health. A number of experimental and epidemiological studies have demonstrated an association between particles with diameters of less than 100 nm and serious adverse health effects (Oberdörster et al., 1995). Recently, many studies in the field of nanomaterial science have focused on the health effects of engineered nanoparticles, which are materials that have at least one dimension between 1 and 100 nm (NIOSH, 2009). The characteristics of nanoparticles can differ from the characteristics of larger particles with the same chemical composition (NIOSH, 2009). For example, both acute instillation and subchronic inhalation studies have shown that ultrafine particles (approx. 20 nm) at equivalent masses access the pulmonary interstitium that was associated with an acute inflammatory response to a larger extent than fine particles (approx. 250 nm) (Ferin et al., 1992). Many possible reasons have been proposed to explain the higher levels of toxicity that are associated with smaller particle diameters. In particular, many studies have suggested that particle surface area is an important parameter determining the toxicity of ultrafine particles (Donaldson et al., 1998; Oberdörster, 2001; Oberdörster et al., 1995; Nakanishi, 2011). Possible reasons which may explain the key role of surface area in the toxicity of ultrafine particles include the findings that large surface areas lead to high concentrations of reactive chemical compounds at deposition sites, causing oxidative stress to cells (Donaldson et al., 1998). Additionally, an increased surface area could also act as a carrier for co-pollutants, such as gases and chemicals, which could attack cells (Oberdörster, 2001). Therefore, it has been suggested that particle surface area distribution could be an appropriate metric for the health effect of ultrafine particles (Giechaskiel et al., 2009; Oberdörster et al., 2005).

The size of atmospheric aerosols ranges from nanometers to tens of micrometers. The aerosol size distributions are frequently observed to be bimodal, with a peak at the submicron level and a second peak at the micron level (Whitby and Sverdrup, 1980). A number of epidemiological studies have demonstrated that there is an association between particulate matter in which 50% of particles have an aerodynamic diameter of less than 2.5 μm ($PM_{2.5}$) and serious adverse health effects, including mortality, morbidity, and respiratory and/or cardiovascular diseases (Dockery et al., 1993; Pope et al., 1995). The smaller part of the bimodal distribution of atmospheric aerosol is the major constituent of $PM_{2.5}$.

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1352-2310/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2013.04.033

It is important to investigate the surface area of atmospheric aerosols as a metric for their adverse health effects; however, few studies have focused on this parameter. This lack of investigation could be due to a number of reasons. For instance, it is difficult to experimentally measure the actual surface area of atmospheric aerosol particles. Although particle number concentrations can be measured using optical methods, and particle mass concentrations can be measured by several reliable methods, including beta-attenuation, light scattering, and tapered element oscillating microbalance, it is difficult to achieve real-time measurement of the surface area of atmospheric aerosol particles. The surface area of the particle can be measured offline using the BET (Brunauer, Emmett and Teller) method; however, the quantity of sample required for this method exceeds several tens of milligrams. This is approximately 1–3 orders of magnitude greater than the amount needed for other ordinary chemical analyses methods. BET analysis also requires samples to be submitted in powder form; however, atmospheric aerosol particles are usually collected for chemical analysis by passing through filters. Consequently, it would be difficult to collect the amounts of atmospheric aerosol samples in powder form required to measure their surface area using the ordinary sampling instruments used for chemical analysis.

Another difficulty associated with examining particle surface area stems from the non-spherical and aggregational nature of the particles being measured. It has been considered that the surface area distribution of atmospheric aerosol particles can be calculated using number or mass size distributions that are easily measured online. This is true if the particle shapes are spherical and nonporous. However, the shapes of actual aerosol particles are non-spherical, and are often porous (Fu et al., 2008; Pipal et al., 2011; Zhao et al., 2011). Moreover, most atmospheric aerosols particles are aggregates and/or agglomerates, consisting of much smaller particles (DeCarlo et al., 2004; Fu et al., 2008; Whitby and Sverdrup, 1980). The surface area of the aggregate/agglomerate is determined by size of primary particles that form the aggregate/agglomerate (Nakanishi, 2011). Therefore, measurement of number/mass size distributions of the aggregate/agglomerate does not correctly predict the actual surface area distribution of the aggregate/agglomerate until the sizes of primary particles that form the aggregates/agglomerates are measured experimentally.

Surface area is often considered to be less important than chemical composition in terms of the health effects caused by atmospheric aerosols particles. Therefore, many studies have considered the chemical composition of aerosols, while neglecting the effect of surface area of atmospheric aerosols. However, many studies have demonstrated that smaller particles with larger surface areas are more toxic than much larger particles with smaller surface areas but the same chemical composition, as mentioned above. It is important, therefore, to investigate the actual surface area of atmospheric aerosols.

Few previous studies have successfully measured the actual surface area of atmospheric aerosols (Bau et al., 2010; Billet et al., 2007). The instruments that are capable of collecting the large amount of atmospheric aerosol samples in powder form required to measure their surface area are not generally available. This study resolved this problem by using several reference materials of atmospheric aerosols that are commercially available in sufficient amounts (several grams) in powder form to carry out an analysis. These reference materials have certified, reference and information values of many chemical species as well as their physical characteristics. The surface area of the atmospheric aerosol particles measured in this study was compared with the given chemical composition of the reference materials. Three kinds of reference materials have been used in this study.

2. Experimental

2.1. Reference materials of atmospheric aerosols particles

The three different reference materials used in this study are described below.

(1) NIST SRM1649a: This SRM, which was made by NIST, USA, was prepared from atmospheric particulate material collected in the Washington, D.C. area using a baghouse filter over a period in excess of 12 months between 1976 and 1977. The particulate material was passed through a 125 μm (120 mesh) sieve in order to remove bag fibers and other extraneous materials.

(2) NIES CRM#28: This CRM, which was made by NIES, Japan, is comprised of atmospheric particulate matter collected on filters in a central ventilating system in a building in Beijing city. The particulate matter was collected over a 10-year period, from 1996 to 2005. The particulate matter was recovered from the filters by mechanical vibration. The recovered material was passed through a 32-μm sieve to remove coarse particles and sterilized using Co-60 irradiation (2.5 Mrad). This CRM was produced in conformance with the ISO Guide 34 (2009).

(3) NIES CRM#8: This CRM, which was made by NIES, Japan, is comprised of atmospheric particulate matter collected over 4-month period from March to June in 1983 from electrostatic precipitators in ventilators connected to a highway tunnel. The electrostatic precipitators were installed between moving fabric filters. This CRM mainly contains much smaller particles than the other two reference materials since fabric filters were able to remove larger particles.

2.2. Particle size distribution

The particle size distribution of the reference materials was determined using the laser diffraction technique (SALD-2300, Shimadzu). Milli-Q ultrapure water (18.2 MΩcm) was used as the dispersion medium, and sodium hexametaphosphate (0.1 wt%) was used as the dispersant agent. Particle dispersion was carried out by ultrasonication (32 kHz, 40 W) for 30 min. For CRM#8, an additional 30 min of ultrasonication (20 kHz, 200 W) was also carried out in order to achieve complete dispersion.

2.3. Specific surface area

The specific surface area of the reference materials was determined using the BET method. Generally, sample pretreatment such as heating under vacuum is needed prior to BET analysis in order to dry up the samples. However, this procedure may alter the original specific surface area of the samples. Nguyen and Ball (2006) reported that the outgassing under high vacuum at 300 °C for 5 h changed the specific surface area of the samples by 9%–67% due to the desorption of gases that originally attached on the particles surface. Therefore, the sample pretreatment condition is important; however, this issue is out of the scope of this study since the effect of pretreatment conditions on the sample specific surface area would be very complicated. In this study, the sample tubes containing approximately 50 mg of the reference materials were outgassed under a vacuum at 60 °C for 5 h prior to analysis, in accordance with a widely-used pretreatment condition for BET analysis (Kanazawa et al., 2012; Yagita et al., 2013). Then nitrogen adsorption data at 77 K were obtained for the samples using a high-resolution gas adsorption analyzer (TriStar 3000, Micromeritics).