Atmospheric Environment 95 (2014) 288–295

Contents lists available at ScienceDirect

Atmospheric Environment

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

Analysis of semi-volatile materials (SVM) in fine particulate matter

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HIGHLIGHTS

- Denuders are recommended to be employed as a standard device in $PM_{2.5}$ instrument.
- Semi-volatile materials contributed largely to $PM_{2.5}$ in a subtropical urban area.
- Beta-gauge overestimated $PM_{2.5}$ for sampling artifacts and aerosol hygroscopicity.
- Both FRM and FDMS–TEOM measurements underestimated $PM_{2.5}$ for SVM loss.
- FDMS was unable to recover the mass of lost SVOMs.

ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form
19 June 2014
Accepted 21 June 2014
Available online 21 June 2014

Keywords:
Urban air quality
Atmospheric aerosols
FDMS–TEOM
Denuder

ABSTRACT

The mass fraction of semi-volatile materials (SVM) in fine particulate matter ($PM_{2.5}$) was investigated at a subtropical urban aerosol observatory (TARO, 25.0 °N, 121.5 °E) in Taipei, Taiwan during August 2013. In particular, an integrated Denuder–FDMS–TEOM system was employed to study the effectiveness of the coupling of FDMS and TEOM instruments. The charcoal and MgO denuders used in this study performed a removal efficiency of 89 and 95% for positive interferences in OC and nitrate measurements, respectively, and did not induce a significant particle loss during the field campaign, suggesting that denuders should be considered as a standard device in $PM_{2.5}$ instrumentation. Analysis on the mass concentration and speciation data found that, as a result of SVM loss, FRM-based measurement underestimated $PM_{2.5}$ by 21% in our case. Coupling FDMS to TEOM significantly improved the bias in $PM_{2.5}$ mass concentration from −25% to −14%. The negative bias in FDMS–TEOM was attributed to the failure of FDMS in recovering the mass of lost SVOMs in $PM_{2.5}$. The results of this study highlight the significance of SVM in a subtropical urban environment, give a warning of underestimated health risk relevant to $PM_{2.5}$ exposure, and necessitate further development of instrument and/or technique to provide accurate ambient levels of fine particulate matters.

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1. Introduction

Epidemiological studies have shown that exposure to particulate matters, particularly the $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm), can inflict adverse health impacts to humans. These atmospheric aerosols are composed mostly of ammonium, nitrate, sulfate, crustal materials, carbonaceous materials (organic matters and elemental carbon), trace metals and water (Pang et al., 2002a; Seinfeld and Pandis, 2006). Trace metals, crustal materials, elemental carbon and sulfate are considered as stable species which can be precisely measured by integrated single filter techniques (Musick, 1999). However, a significant fraction of the particulate matters consists of semi-volatile species that can exist in both gas and particle phases, which partition depending on a number of conditions such as temperature and relative humidity. Previous studies indicated that semi-volatile materials (SVM) comprise mostly of NH_4NO_3, semi-volatile organic matters (SVOMs) and water, which could cause both "positive" and "negative" artifacts in the measurements involving single filter techniques (Eatough et al., 2003a,b; Wilson et al., 2006; Solomon and Sioutas, 2008). Negative bias arises from the loss of SVM during sampling particularly due to the increase in the temperature of the air stream, pressure drop across the filter, and changes in the concentration of the gas phase compounds at equilibrium (Grover et al., 2008). Positive bias on the

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http://dx.doi.org/10.1016/j.atmosenv.2014.06.046
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other hand originates from the adsorption of the gas phase SVM (e.g., nitric acid and VOCs) from the air stream (Pang et al., 2002a,b).

Water in aerosols contributes significantly to the physical and chemical properties of particulate matters. For instance, water could increase or decrease the lifetime of aerosol particles through altering the size distribution. Furthermore, the presence of water in the particulate phase may change the phase partitioning of other semi-volatile components, thus changing the chemical composition of aerosols (Ansari and Pandis, 1999). However, limited studies have accounted the presence of water in aerosols due to its complexity in measurement, and its dependence on relative humidity (RH) as well as on the composition of aerosols (Lee and Chang, 2002; Khlystov et al., 2005).

Another significant contributor to the mass loading of the semi-volatile particulate matters is ammonium nitrate, particularly in highly urbanized areas (Adams et al., 1999; Allegrini et al., 1994; Yu et al., 2005). The formation of ammonium nitrate is based upon the reaction of the gaseous nitric acid (HNO_3) and ammonia (NH_3) in the ambient air (Yu et al., 2005).

$$NH_{3(g)} + HNO_{3(g)} \rightarrow NH_4NO_{3(p)} \quad (1)$$

This reaction is reversible and dependent on the temperature and RH of the ambient air. At low temperature and high RH conditions such as during the night, the formation of the particulate nitrate is highly favorable. The reverse happens during daytime where high temperature is usually observed (Stelson and Seinfeld, 1982; Yu et al., 2005).

The gas/particle conversion of semi-volatile organics also highly attributes to the bias in single filter measurements. Interestingly, a significant portion of the organic materials can be accounted to SVOMs where up to 60–90% of its mass was reported to be lost during sampling (Mader et al., 2001; Pang et al., 2002b). It is generally recognized that SVOMs partition to the gas phase during daytime and condense back to particulate phase at night due to decrease in ambient temperature (Fan et al., 2004).

In measuring SVM, denuders have been widely utilized in aerosol speciation measurement to eliminate positive artifacts in the concentration of specific species. Charcoal denuders, for instance, have been extensively utilized in scrubbing organic gases from sampling stream (Subramanian et al., 2004). For specific reactive gases of interest (e.g., nitric acid), coating of substrates such as MgO on the wall of denuders can uptake the gaseous species by chemical adsorption (Baron and Willeke, 2005). However, to date, denuders have not been included in standard instrumentation of $PM_{2.5}$ mass measurement.

With the inclusion of semi-volatile mass fraction in mass measurements and removal of interferences, the effectiveness of the PM standard and health risk assessment would be enhanced due to accurate epidemiological identification and quantification of some of the components of fine particles which are previously unaccounted (Eatough et al., 2003b). In this light, this study intends to investigate the mass fraction of SVM in $PM_{2.5}$ in Taipei, Taiwan, a typical subtropical urban area. Mass concentration and speciation measurements were conducted concurrently. In particular, a filter dynamic measurement system–tapered element oscillating microbalance (FDMS–TEOM) was employed and evaluated. FDMS–TEOM is a recently developed instrument that is designed to measure mass concentration of ambient particulate matters consisting both nonvolatile and semi-volatile species (Grover et al., 2005). However, evaluation upon the effectiveness of coupled FDMS–TEOM is rather limited. Because the FDMS does not include denuders, the "reference signals" are subjected to both positive and negative interferences. Therefore, in this study, denuders are coupled to a standard FDMS–TEOM to remove positive artifacts and, therefore, allow the "reference signals" serving as a measure of negative artifacts associated with traditional single-filter measurements of aerosol mass concentration. Moreover, besides ammonium nitrate and SVOMs, unbound water as part of SVM was also accounted using ISORROPIA II, a thermodynamic equilibrium model for aerosol system (Fountoukis and Nenes, 2007).

2. Experimental methods

2.1. MgO and charcoal denuder efficiency analysis

The denuder system in this study consists of two activated carbon (charcoal) monolith denuders (Mast Carbon International Ltd., UK) and one MgO-coated diffusion denuder (Met One Instruments Inc., USA). Each charcoal denuder is 80 mm long and 30 mm in diameter with 230, 1 mm^2 channels/sq inch. The MgO-coated denuder is that employed by the Met One Super-SASS Speciation sampler for scrubbing nitric acid and other related nitrogenous compounds in the air stream. Before integrating the denuders to the FDMS–TEOM, the efficiency of each charcoal and MgO denuder was evaluated following the experimental setup of Subramanian et al. (2004). The design for removal efficiency analysis used in this study is illustrated in Fig. 1. All the filters used had 47 mm diameter. Flow rate utilized was 6.7 LPM in this analysis. The denuder efficiency analyses for both denuders were done for five days continuously.

2.2. Aerosol sample collection

This study was conducted at the Taipei Aerosol and Radiation Observatory (TARO), which is located at the Atmospheric Science Building of National Taiwan University (NTU) (25.0 °N, 121.5 °E) in Taipei, Taiwan. TARO is situated in the downtown area of Taipei Basin, thus is capable of providing representative data for aerosols in a subtropical urban area. Detailed description of the TARO can be found elsewhere (Cheung et al., 2013). Given the substantial emissions of air pollutants from automobiles in downtown Taipei, elevated levels of nitric acid, organic gases and other gaseous compounds that may have contribution to the formation of semi-volatile materials are expected. Daily aerosol samples were collected continuously from August 1 to 16, 2013, starting from 14:00 to 12:00 (local time) of the following day. Note that, during the sampling period, ambient temperature reaching as high as 39.3 °C was observed on August 8, which was recorded as the highest since the Central Weather Bureau of Taiwan started 117 years ago (Shan and Mo, 2013).

During this study, one FDMS–TEOM (Model 1405, Thermo Fisher Scientific), one Super-SASS speciation sampler (Met One Instruments Inc., USA) and two FRM $PM_{2.5}$ samplers (PQ-200, BGI Inc., USA) were collocated at the sampling site. Super-SASS consists of four independent sampling channels designed for simultaneous measurements for various chemical and/or physical properties of aerosols. The configuration of the filters and denuders loaded in the instrument is given in Fig. 2. Both PQ-200 samplers were equipped with very sharp cut cyclone (VSCC, BGI Inc., USA) for the collection of fine particulate matter ($PM_{2.5}$). To eliminate possible contamination associated with filters, quartz fiber filters (Tissuquartz, 47 mm in diameter, Pall Corp) were pre-combusted at 900 °C for 4 h before sampling, while Nylon filters (NylaSorb, 1.0 μm pore size, 47 mm in diameter, Pall Corp) were washed with Milli-Q water (Merck Millipore) and purged with clean air until dry. MgO denuders were soaked and cleaned with Milli-Q water and purged with clean air overnight. The denuders were housed in a stainless-steel casing, designed specifically for the dimensions of the

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