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Q1 Development of an on-line measurement system for water-soluble organic matter in $PM_{2.5}$ and its application in China

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ABSTRACT

Water-soluble organic matter (WSOM) represents a critical fraction of fine particles ($PM_{2.5}$) in the air, but its changing behaviors and formation mechanisms are not well understood yet, partly due to the lack of fast techniques for the ambient measurements. In this study, a novel system for the on-line measurement of water-soluble components in $PM_{2.5}$, the particle-into-liquid sampler (PILS)–Nebulizer–aerosol chemical speciation monitor (ACSM), was developed by combining a PILS, a nebulizer, and ACSM. High time resolution concentrations of Q3 WSOM, sulfate, nitrate, ammonium, and chloride, as well as mass spectra, can be obtained with satisfied quality control results. The system was firstly applied in China for field measurement of WSOM. The mass spectrum of WSOM was found to resemble that of oxygenated organic aerosol, and WSOM agreed well with secondary inorganic ions. All evidence collected in the field campaign demonstrated that WSOM could be a good surrogate of secondary organic aerosol (SOA). The PILS–Nebulizer–ACSM system can thus be a useful tool for intensive study of WSOM and SOA in $PM_{2.5}$.

Introduction

Water-soluble organic matter (WSOM) is operationally defined as the fraction of particulate organic matter that can be extracted by water. WSOM represents a significant fraction (10–70%) of the fine aerosol particle mass in the atmosphere (Andrews et al., 2000). There is increasing interest in the ability of WSOM to alter a particle's hygroscopicity (Fors et al., 2010) and to act as cloud condensation nuclei (Padró et al., 2010). These processes could potentially impact regional air quality and the global climate. The composition of WSOM is highly complicated due to a multitude of molecular forms, sources, and reactivity. According to Chow et al. (2008), WSOM composition includes (1) sugars and their derivatives, (2) mono- and dicarboxylic acids, (3) amino acids, (4) polycarboxylic acids, and (5) humic-like substances (HULIS). Techniques that provide information on the molecular composition could provide unique insights into the sources and the formation processes of WSOM in ambient aerosols.

Most WSOM studies have been based on filter sampling, which offers measurement results with low time resolution, such as 24 hr, although the chemical complexity of WSOM, and fast variations of meteorological conditions, necessitate highly time-resolved on-line analysis. Sullivan et al. (2004) presented an instrument for on-line continuous measurement of water-soluble organic carbon (WSOC) by combining a particle-into-liquid sampler (PILS) with a total organic carbon (TOC) analyzer. With this method, WSOM is collected into

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purified water by the PILS. The resulting effluent is filtered and the organic carbon content is quantified by the TOC analyzer. This system provides continuous six-minute integral measurements with a detection limit of 0.1 μg C/m^3. Since the method was first introduced, the PILS–TOC has become the ideal choice for on-line measurements of WSOC (Weber et al., 2007; Timonen et al., 2010) because the PILS–TOC improves time resolution through automatic sampling and reduces sampling artifacts associated with the filter method and the contamination risk associated with handling and storage of filter samples. However, this system does not provide additional information about the molecular composition of WSOM beyond the highly time-resolved total WSOC concentrations. Recently, Cerully et al. (2015) reported one sampling line in which submicron particles (PM_1) are not directed to a high-resolution time-of-flight aerosol mass spectrometer (HR–ToF–AMS) but through a PILS first, *i.e.*, the PILS–AMS system. The PILS effluent is then filtered and nebulized to aerosols again, which are later dried and finally directed to the AMS for detection. In this way, the AMS provides quantitative data on water-soluble inorganic and organic PM_1 with high time resolution and information about WSOM mass spectra and elemental composition.

In this study, a new system was developed by combining a PILS, a nebulizer and an aerosol chemical speciation monitor (ACSM), *i.e.*, the PILS–Nebulizer–ACSM system, and several modifications and technical parameters were tested. Compared with the PILS–TOC, the PILS–Nebulizer–ACSM can provide not only WSOM mass concentrations, but also detailed information about WSOM compositions. When compared to the PILS–AMS, the PILS–Nebulizer–ACSM is better for long-term deployment because of the lower cost and easier operation of ACSM. In addition, the PILS–Nebulizer–ACSM in this study was designed for measurement of $PM_{2.5}$ rather than PM_1, because the size distribution peak of WSOM previously measured in China was just around 1 μm (Huang et al., 2006) and the design for $PM_{2.5}$ is more suitable for understanding the full picture of WSOM in fine aerosol particles. The PILS–Nebulizer–ACSM system is able to provide quantitative data on water-soluble, inorganic and organic components of $PM_{2.5}$ with high time resolution and rich information on WSOM mass spectra and elemental compositions, greatly supporting investigations into the sources and formation mechanisms of WSOM.

1. Experimental method

1.1. Description of the PILS–Nebulizer–ACSM system

A schematic diagram of the instrument setup is shown in Fig. 1. The system consists of six main parts, namely a $PM_{2.5}$ size selector, three denuders in series, a PILS, a nebulizer, two dryers in series, and an ACSM. A $PM_{2.5}$ size selector was used at the top of the sampling line to cut off particles whose aerodynamic diameter was greater than 2.5 μm. After the selector, the sample flow (16.7 L/min) was directed to three denuders. A parallel-plate carbon filter denuder (Sunset Laboratory Inc., USA) and two honeycomb denuders coated with Na_2CO_3 and citric acid, respectively, were used to remove gaseous compounds like volatile organic compounds (VOCs),

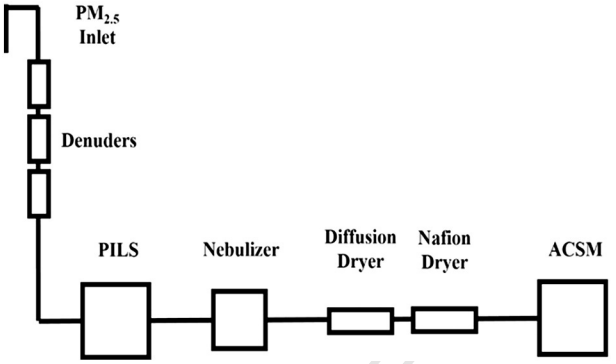

Fig. 1 – Schematic of the PILS–Nebulizer–ACSM system.

ammonia, and sulfur dioxide. After the denuders, the aerosols were directed to the PILS (Metrohm Peak Inc., Switzerland) and then the water-soluble components in aerosols were collected in purified water (18.2 M, TOC < 4 ppbv, Millipore, USA). The design and operating principle of the PILS have been described in detail by Orsini et al. (2003). The PILS effluent continuously passed through a debubbler and a 0.45 μm liquid filter and was pumped onto the face of the piezoelectric transducer of the ultrasonic nebulizer (U-5000AT+, Cetac Technologies, USA), where it was converted to a fine, dense aerosol. The nebulizer gas flow (79% N_2 and 21% O_2, 750 cm^3) transported the wet aerosol through a diffusion dryer and a Nafion dryer to reduce humidity to below 30%. The PILS effluent output was a dry, analyte-laden aerosol, which was directed to the ACSM (Aerodyne Research Inc., USA) to enable simultaneous high time resolution (15 min) measurements of WSOM, sulfate, nitrate, ammonia, and chloride as well as the WSOM mass spectrum. The design and operating principle of ACSM have been described in detail by Ng et al. (2011).

1.2. System tests

1.2.1. Particle size

It should be noted that ACSM measurements are typically referred to as PM_1 measurements because particles with vacuum aerodynamic diameters of 1 μm are transmitted through the inlet at an efficiency of ~30–50% depending on the exact details of the lens assembly and sampling pressure (Liu et al., 2007). Thus, only those particles with an aerodynamic diameter less than 1 μm can be detected by the ACSM. The 100% transmission efficiency of particles in the lens occurs in the size range of 70–500 nm (Canagaratna et al., 2007). We introduced a scanning mobility particle sizer (SMPS, TSI, USA), temporarily replacing the ACSM in the instrument to scan the size of the aerosol particles produced by the nebulizer using PILS effluents and the NH_4NO_3 standard solutions of 0.1–3 mg/L, which were equivalent to 1–70 μg/m^3 ambient particle mass concentration. These solutions were directly pumped into the Nebulizer–SMPS for detection, independent of the PILS. As in Fig. 2, the scanning results showed that the most part of the size distribution of particles produced was in the aerodynamic diameter range of 70–500 nm, consistent with the size range of the 100% transmission efficiency for the ACSM inlet lens.

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