



Characterization of the volatile fraction of laboratory-generated aerosol particles by thermodenuder-aerosol mass spectrometer coupling experiments

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ABSTRACT

An aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) combined with a thermodenuder (TD) was used to investigate laboratory-generated aerosol particles with regard to their volatility and chemical content. The performance of the setup was tested first by using ammonium sulfate particles. Organic compounds have been measured including humic acid, fulvic acid, succinic acid and its disodium salt, 2-methylsuccinic acid, fumaric acid, α -ketoglutaric acid, and glutaric acid. Among them, humic acid, fulvic acid, and disodium succinate show a non-volatile fraction at 300 °C, while the other organic compounds are more volatile. Comparisons of mass spectra at different temperatures showed that significant differences in mass spectra of humic and fulvic acids are observed, indicating that their molecules changed during or after volatilization. At lower temperatures, the changes in humic acid are more likely due to the evaporation of small organic molecules or decomposition of aliphatic groups. The mass losses of the CO₂⁺ fragment for both humic and fulvic acids at higher temperatures may arise from decarboxylation processes. The different mass spectra for humic and fulvic acids before and after TD also suggest that one should be careful in interpretation of volatility measurements because some molecule structures may change after being heated, especially for the non-volatile multifunctional compounds.

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1. Introduction

Atmospheric aerosol particles influence the global climate directly by scattering solar radiation and indirectly by acting as cloud condensation nuclei (CCN) (Charlson, Langner, Rodhe, Leovy, & Warren, 1991; Haywood & Boucher, 2000), and also negatively affect human health (Pope, 2000; Samet, Dominici, Curriero, Coursac, & Zeger, 2000). These aerosols can compose a significant semi-volatile fraction including both inorganic (such as NH₄Cl and NH₄NO₃) (Seinfeld & Pandis, 1998) and organic species (Kanakidou et al., 2005). The partitioning of semi-volatile compounds between the gas and particulate phases is directly related to the formation of atmospheric particles (Kanakidou et al., 2005; Pio & Harrison, 1987). On the other hand, aerosol particles also consist of non-volatile components. For example, elemental carbon, which originates from combustion processes, contributes to a substantial fraction of particles in continentally polluted environments (e.g. Huang, Yu, He, & Hu, 2006). Kalberer et al. (2004) found that the non-volatile fraction of secondary organic aerosol (SOA) produced by photooxidation of aromatic compounds in a reaction chamber is a polymerization product. In a field measurement, Wehner et al. (2005) observed a non-volatile fraction in the range of newly formed particles, but the composition of these particles was not identified yet. The real-time

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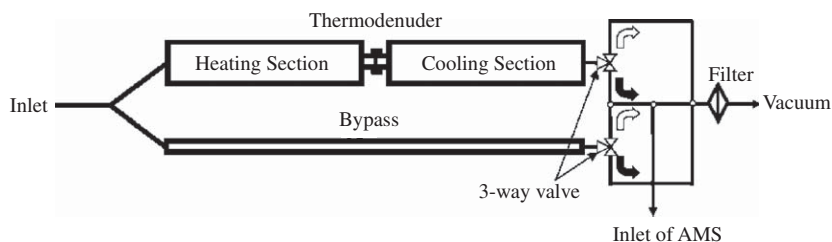


Fig. 1. Schematic diagram of the setup for AMS coupled with thermodenuder.

characterizations of both volatility and chemical composition are thus helpful to comprehensively understand the sources of organic aerosols in the atmosphere.

Volatility measurements have been widely performed to investigate exhaust particles (e.g. Biswas, Ntziachristos, Moore, & Sioutas, 2007; Kuhn, Biswas, & Sioutas, 2005; Sakurai et al., 2003; Wehner, Philippin, Wiedensohler, Scheer, & Vogt, 2004). Recently, they were also used to gain insights into the mechanism of SOA formation (Jonsson, Hallquist, & Saathoff, 2007; Kalberer et al., 2004; Stanier, Pathak, & Pandis, 2007). The most common device for volatility measurements is the thermodenuder (TD). Its design relies on the evaporation of specific chemical components over specific temperature (Burtscher et al., 2001; Wehner, Philippin, & Wiedensohler, 2002). A combination of TD and aerosol size spectrometer can examine the change in particle size distribution due to the removal of volatile species (Ehn et al., 2007; Wehner et al., 2005). A TD can also be placed upstream of a humidifier to measure changes in the hygroscopic behavior of particles as volatile components are removed (Johnson, Ristovski, & Morawska, 2004). Another technique, which has much in common with TD, is the volatility tandem differential mobility analyzer (VTDMA). It is utilized to measure the size distribution of non-volatile fraction of monodisperse particles or their mixing state (Orsini, Wiedensohler, Stratmann, & Covert, 1999; Paulsen, Weingartner, Alfarra, & Baltensperger, 2006; Philippin, Wiedensohler, & Stratmann, 2004). These instruments, in which a TD is applied, are able to provide indirect information about the chemical composition of particles (Jennings and O'Dowd, 1990), but can not directly detect the changes in their chemical composition after being heated.

Aerosol mass spectrometers (AMS), which are increasingly being applied to study atmospheric aerosol composition, can provide real-time size resolved chemical composition and mass concentration analysis of non-refractory particle material with a high time resolution and a high sensitivity (DeCarlo et al., 2006). By combining the AMS with the TD, the set-up can provide both volatility and chemical information on aerosol particles, simultaneously. Comparisons of mass spectra derived from the AMS before and after the TD can characterize both volatile and non-volatile fraction of particles at different evaporation temperatures and examine if molecules change during the process of being heated or do not completely evaporate. Previously, thermodenuder-aerosol mass spectrometer coupling experiments mainly focused on the field campaign was performed by Huffman et al. (2006). In our study, an AMS was combined with a TD to measure laboratory-generated organic aerosol particles. The thermal analysis in the laboratory of organic compounds which might be of atmospheric relevance may help to find potential candidates for non-volatile material contributing to the particle growth reported by Wehner et al. (2005).

2. Experimental method

2.1. Description of the setup for AMS combined with the TD

Fig. 1 shows the schematic diagram of the setup for AMS combined with the TD. The TD consists of a heating section following by a cooling section. The temperature of the heating section can be set from room temperature (25 °C) to 300 °C. The cooling section is filled with activated carbon to remove evaporated material and to cool the sample to room temperature. The TD was operated at a flow rate of 0.61 min^{-1} and at temperatures up to 300 °C. The residence time of particles in the heating section was approximately 9 s. A detailed description of the TD is given in Wehner et al. (2002). Due to diffusional and thermophoretic processes, particle losses occur within the TD. The penetration efficiency of the TD used in our study was measured by Wehner et al. (2002). Their results showed that penetration efficiency increases with increasing particle size at a given temperature, and is nearly constant for particles larger than 80 nm. The particle mass size distributions derived from AMS in this study centered at mobility diameters larger than 80 nm (see Section 2.2). Therefore, the particle mass losses at different temperatures were estimated according to transmission efficiency of 80 nm particles reported in Wehner et al. (2002). The penetration efficiency was 98% and 85% for 25 and 280 °C, respectively.

A nebulizer was used to generate particles from a solution of selected compounds diluted in ultra-pure water (18.2 M Ω cm at 25 °C; Milli-Q Academic, Millipore, USA). The particles were dried by mixing with pure dry air and passed through a diffusion drier filled with silica gel. The sampled air produced by nebulizer was split into two lines. One of them passed through the TD, and another transited a stainless steel tubing (bypass), which was placed parallel to the TD. After the TD and bypass, the flow direction was controlled by two 3-way valves, as shown in Fig. 1. By changing the flow direction, the particles entering into the

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