Thermal Desorption Chemical Ionization Mass Spectrometer for Ultrafine Particle Chemical Composition

D. Voisin,1 J. N. Smith,2 H. Sakurai,3 P. H. McMurry,3 and F. L. Eisele2,4

1 Université de Provence, Marseille, France
2 National Center for Atmospheric Research, Boulder, Colorado
3 Mechanical Engineering Department, University of Minnesota, Minneapolis, Minnesota
4 EAS, Georgia Institute of Technology, Atlanta, Georgia

A thermal desorption chemical ionization mass spectrometer has been developed for real time, quantitative chemical analysis of ultrafine particles. The technique combines recently developed nanoparticle separation and collection techniques with highly sensitive chemical analysis provided by selected ion chemical ionization mass spectrometry. Sensitivity tests using laboratory-generated ammonium sulfate particles in the diameter range 10–16 nm show that sulfate and ammonium can be quantified with as little as 1 pg of collected aerosol mass. Such sensitivity makes this instrument suitable for real time measurements of the chemical composition of sub-10 nm particles reported recently from nucleation events.

INTRODUCTION

The majority of ultrafine particles in the atmosphere (with diameters up to 100 nm) originate in combustion processes and in gas-to-particle conversion. These processes and the ensuing growth mechanism control the number and size of particles produced, which ultimately determine aerosol lifetimes and cloud condensation nuclei production. As they are highly dynamic processes, they have evaded study for a long time. In the last decade, tremendous improvements have been made on the detection and sizing of aerosol, so that measurements of size distributions down to 3–4 nm on a time scale of minutes are now common (McMurry 2000). This has made it possible to investigate nucleation and growth processes of aerosols in the atmosphere (see, for example, Clement et al. 2001; McMurry et al. 2000). Such studies have focused on aerosol physical characterization, primarily particle size-distributions. A major problem currently stalling research on chemical mechanisms responsible for particle nucleation and growth is the absence of online techniques for real-time measurements of the size-dependent chemical composition of ultrafine aerosol. Current methods, based on multistage impactors and offline analysis (Cass et al. 2000), lack the time resolution or sensitivity needed to study these highly dynamic processes.

Recently, a number of instruments based on mass spectrometry have been developed for fast online measurements of the size-dependent chemical composition of aerosols (Suess and Prather 1999 and references cited therein). These instruments can be distinguished by the method by which particles are volatilized and the resulting gas-phase compounds ionized. Many of these instruments use high-powered pulsed lasers to volatilize and ionize the compounds within single particles. These laser-based instruments have made significant progress towards analyzing aerosols in the nanometer size range through the use of aerodynamic and electrostatic lenses to create a beam of particles, which are then volatilized by a freely firing desorption/ionization laser (Kane et al. 2001; Phares et al. 2002; Reents and Ge 2000). The current minimum sensible aerosol diameters for these laser-based techniques are ~20 nm for the instruments that obtain molecular composition information (Kane et al. 2001; Phares et al. 2002), and ~10 nm for the atomic composition instrument of Reents and Ge (2000). The challenges that still exist for the aerosol molecular composition instruments include excessive fragmentation of organic compounds, low hit rates for aerosols smaller than ~50 nm, and unpredictable vaporizing/ionizing conditions that make quantitation a challenge. Another class of instruments uses thermal desorption to volatilize the particles followed by a separate ionization step (Jayne et al. 2000; Tobias et al. 2000). The more stable evaporation and ionizing processes enable these instruments to be quantitative, with reported sensitivities of ~250 μg/m³ (signal averaging mode) for the instrument of Jayne et al. and 0.1–1 μg/m³ for the instrument of Tobias et al. As in the case of the laser-based instruments, current...
minimum sensible diameter, approximately 40 nm, is limited by the minimum size that can be transmitted through the aerodynamic lenses used in transmitting particles to the thermal desorption region. None of the current online analytical techniques are capable of measuring the molecular composition of atmospheric aerosol in the 4–10 nm diameter range, the size range that is characteristic of newly formed aerosol.

We describe here an instrument with the sensitivity needed to measure the molecular composition of sub-10 nm diameter aerosols at ambient concentrations in the atmosphere. The technique, called thermal desorption chemical ionization mass spectrometry (TDCIMS), builds on our experience in developing highly sensitive selected ion chemical ionization mass spectrometers for the detection of atmospheric gas-phase compounds at concentrations below $10^5$ molecules/cm$^3$ (Mauldin et al. 1999).

In our experimental setup, described in detail below, aerosols are charged and then collected by electrostatic deposition on a metal filament. Then the filament is slid into a chemical ionization region where it is resistively heated to evaporate the aerosol. The desorbed molecules are ionized at atmospheric pressure by proton transfer with protonated water clusters or oxygen anions. Ions are then transferred to a triple quadrupole mass spectrometer for mass analysis.

**INSTRUMENT DESCRIPTION**

The instrument (Figure 1) is made of an electrostatic precipitator for collecting charged particles, an evaporation-ionization chamber, and a triple quadrupole mass spectrometer equipped with a collision-induced dissociation (CID) chamber. The CID chamber is used to strip clusters down to their core ion before they are mass, or tandem mass, analyzed. The tandem mass spectrometry capability is useful for analyzing particles containing mixtures of organic compounds. The system is equipped with a bipolar charger and a nanometer aerosol differential mobility analyzer (nano-DMA) (Chen et al. 1998) at the inlet to charge and select particles of a given size, and with a condensation particle counter at the outlet, which is used to quantify the collected aerosol mass.

**Electrostatic Precipitator**

The electrostatic precipitator consists of a 6 cm inside diameter, 30 cm long coaxial collection tube with a central ceramic rod holding a metal filament used to collect particles (Figure 1). An 8 sl/min flow of air containing charged ultrafine particles is continuously drawn in through the outer annulus. The inner tube (3.5 cm OD) extends 25 cm into the collection tube and is flushed with 2 sl/min of ultrapure nitrogen that protects the collection filament from contamination by gaseous compounds present in the particle-laden air flowing in the outer annulus. The combined flow is then drawn radially out through a slot in the outer wall, insuring flow symmetry at the outlet. In the collection position, the metal filament protrudes 0.8 cm from the end of the inner tube. The exact position is set within 0.02 cm by a computer-controlled linear actuator that also rapidly slides the filament from the collection position into the evaporation-ionization chamber for analysis. In the collection mode, an electric field is maintained between the outermost stainless steel cylinder and the filament to move charged particles from the sample airflow through the nitrogen sheath gas and onto the filament. The collection potential on the filament is thus usually set to ~4000 V, balancing high collection efficiency with the potential for corona emission around the filament at excessive voltages. During collection, particles on the wire are exposed to purified nitrogen and are thus susceptible to volatilization. Although not a significant problem in the current study, which focuses on ammonium sulfate aerosol, particle volatilization is clearly an important factor in analyzing organic aerosols and may be minimized by controlling the temperature and/or humidity of the collection region.

**Evaporation-Ionization Chamber**

The evaporation-ionization chamber is a cylindrical chamber made of 4 stainless steel rings separated by electrical insulators. The central ring is coated with a radioactive material ($^{231}$Am) emitting $\alpha$ particles that ionize the buffer gas mixture to form nitrogen and oxygen ions that subsequently react to form $\text{H}_3\text{O}^+$, $\text{O}_2^-$, and $\text{CO}_3^{2-}$ as the primary stable ions. These ions will then react with the compounds evaporated from the aerosol.

Figure 1. Diagram of thermal desorption chemical ionization mass spectrometer source, with filament in collection mode. Dashed line shows filament in sample desorption and analysis mode.
The ion source assembly is encapsulated in a heating ribbon and heated to \( \sim 70^\circ C \) to avoid condensation of the evaporated material back onto the walls. Three nitrogen flows are fed into the chamber. The first one (0.03 sl/min) flushes the ionization chamber, pushing evaporated compounds slowly towards the vacuum system aperture. This flow is kept small, as is the volume of the evaporation-ionization region (2.5 ml), in order to minimize dilution of the evaporated material and to increase its residence time in the ionization region. As the vacuum system pumps a total flow of 0.13 sl/min, 0.1 sl/min are added to this first flow in front of the ionization region. The third flow (0.6 sl/min) is directed towards the collection region, isolating the ion source from the electrostatic precipitator and the sample air.

The collection filament is made of nichrome (90% Ni/10% Cr) and can be resistively heated by pulsing a known current through it. Filament temperature versus current was measured in a separate test by spot welding a thermocouple to the tip. Controlling the current leads to a known temperature with an accuracy of \( \pm 5^\circ C \). When in evaporation mode, the filament is located in the center of the ionization chamber (Figure 1). The filament and the rings that comprise the chamber are electrically biased to force ions to travel axially from the ion source to the vacuum entrance aperture. These and all mass spectrometer lenses are computer controlled, allowing automated switching from positive to negative ion measurement. In the current study, positive ion mode is used to detect NH\(_3\) produced by the evaporation of ammonium sulfate, which readily reacts with H\(_3\)O\(^+\) water clusters to create NH\(_4^+\). It will also be used in the future to detect oxygenated and unsaturated organics, known to react quite effectively with H\(_3\)O\(^+\) (Lindinger et al. 1998). Negative ion mode is used to detect sulfuric acid, from the thermal dissociation of ammonium sulfate and from evaporation of free sulfuric acid in the aerosol. In the future, the negative ion mode may also be used to detect organic acids, which are known to be present in ultrafine aerosols (Cass et al. 2000).

In the current investigation, a triple quadrupole mass spectrometer (ABB Inc., Pittsburgh, PA) is used for mass analysis. Mass accuracy and resolution were adjusted to within 1 amu and 1 amu FWHM, respectively. Tandem mass spectrometry experiments were not performed in the current investigation since the compounds present in the aerosol were relatively simple. The capability of tandem mass spectrometry for elucidating structure of complex molecules will be crucial for future planned investigations of organic aerosol.

**EXPERIMENT**

Singly charged particles were produced using a commercial electrospray aerosol generator (TSI, Inc., model 3480), and a solution of 10 mg ammonium sulfate in 10 ml of water containing 10 mM ammonium acetate to enhanced solution conductivity for stable spray operation. These particles were size selected by a nano-DMA and the resulting monodispersed, singly charged ammonium sulfate particles sent to the TDCIMS. A condensation nucleus counter (CNC; TSI, Inc., model 3020) connected to the outlet of the electrostatic precipitator is used to determine the collected aerosol mass by the following procedure. We noted the difference between measured concentration during collection compared to that before and after collection and correct this difference by the efficiency by which particles are transferred out of the collection region to the inlet of the CNC. This efficiency was measured in a separate set of experiments at the same flow rates and concentrations as those used in this study. An additional scanning mobility particle sizer (TSI, Inc., model 3080N) was used to regularly check the size distribution and number concentration of the charged ultrafine particles sent to the system and to confirm that no multiply charged particles were present. For these tests, the filament became contaminated if it protruded from the sheath tube at distances greater than 8 mm. At this distance, collection efficiency was ca. 60% for 10 nm particles. Future improvements to the design will allow us to extend the filament further and thus lead to greater collection efficiencies.

A typical measurement sequence is as follows: the filament is first heated to 400\(^\circ\)C for 1 min to clean it before starting a new analysis; after waiting for the filament to cool, it is then set to its collection position and a collection voltage applied to it for a given time. The collection voltage is turned off and the filament slid into the analysis position, where it is heated to 100\(^\circ\)C for 60 s to evaporate the aerosol. Total analysis time is 2.5 min added to the time allowed for aerosol collection. Figure 2 shows typical ion peaks for ammonium sulfate aerosol. In the positive ion mode, a clear signal can be seen for NH\(_4^+\) (18 amu) when the filament is heated in the ionization chamber (Figure 2a). The peak of evaporated ammonium persists for less than 5 s and reaches a maximum of 1990 counts per second above a 320 counts per second background, corresponding to a signal to noise ratio of 6.2 (calculated as the peak height divided by the standard deviation of the background). The collected aerosol mass for the peak in Figure 2a is 3.2 pg, corresponding to 14 nm particles collected at a concentration of 2750 cm\(^{-3}\) for 60 s. Tests were also performed in negative ion mode to establish instrument response for sulfate in ammonium sulfate aerosols. A peak is observed for bisulfate (the stable form of sulfate in the gas phase) when the filament is heated in the ionization chamber (Figure 2c). Figure 2c shows the result for 10 nm particles being collected at a concentration of 4300 cm\(^{-3}\) for 120 s, resulting in a collected aerosol mass of 1.8 pg. In the case of bisulfate ion, Figure 2c shows two peaks arising from sample desorption and ionization. The presence of two peaks suggests two separate mechanisms for the formation of bisulfate from ammonium sulfate aerosol. The signal-to-noise ratio for the bisulfate trace in Figure 2c is 60.

Systematic tests were made to insure that the observed signal was indeed associated with collected aerosols. In the first test the filament was left to sit in the sheath flow in collection position, with no voltage applied to it and with the ultrafine particle-laden sample air flowing around it. The resulting traces for NH\(_4^+\) and HSO\(_4^-\) are shown in Figures 2b and 2c, respectively. These “background peaks” arise from contaminated air.
that contacts the filament, either while it is in collection position, in transit, or just after the high-current cleaning pulse is applied when thermophoretic flows may be present. These tests show that the actual peaks obtained after collecting particles will have a small contribution from other sources that must be subtracted if one wishes to correlate ion peak area with the concentration of the neutral species in the aerosol. To insure that this background peak is from gas phase contamination, filtered room air was sampled and the collection voltage applied as usual before sample analysis. This gave peaks that are similar to the background peaks described above, indicating that the contamination is not caused by aerosols. Further tests have shown that these background signals can be minimized by increasing the flow of clean sheath gas surrounding the wire and by positioning the wire so that it does not protrude as far from the end of the sheath tube.

A series of tests were also made to compare ion peak integrated area to the collected aerosol mass. For these experiments, ammonium sulfate aerosols were generated and size-classified with the nano-DMA into 14 and 10 nm aerosols for measurements of ammonium and sulfate, respectively. Collection times were varied from 15 s to 5 min in order to vary the collected aerosol mass. Plots of integrated ion peak area versus collected aerosol mass are shown in Figure 3. In the plot, uncertainties associated with generating ammonium sulfate particles of known diameter were primarily responsible for the error in the total aerosol mass. The uncertainty in the measurement of the integrated peak area arises from the manual integration scheme that we employed for this study. The integrated peak areas shown in Figure 3 are the net areas obtained by subtracting the background peak areas from that of the collected aerosols. The data thus represent the chemical compounds present only in the aerosol phase. For both ammonium and sulfate, the trends are linear. In the case of bisulfate (Figure 3b), a slight departure from linearity can be seen for collected aerosol mass below 1 pg. Although the cause of this departure from linearity is not known, since it occurs near the detection limit we can state an effective detection limit (1 pg) that corresponds to the lowest mass for which fully linear calibration is observed.

During the period of this study no detectible change in instrument calibration was observed under identical operating conditions. Some long-term variations in calibration have been observed over the course of months, which may be related to the aging of the collection wire. These effects are the focus of current investigations.
ANALYSIS AND CONCLUSION

The TDCIMS instrument is able to detect ammonia and sulfuric acid vapor at high sensitivity, while its repeatability makes it suitable for quantitative chemical analysis of ultrafine particles. Its unique features include sensitivity to a few picograms of collected aerosol and a minimum detectable aerosol diameter of 4 nm, which is limited by diffusive losses in the detector. Using the aerosol sampling flow rates reported here (8 sl/min) and a collection time of 10 min, the results of this study suggest sensitivity to ambient aerosol mass concentrations of \( \sim 50 \text{ pg/m}^3 \). This detection limit is based on a 40% charging efficiency for particles of 10 nm diameter, the measured efficiency of our unipolar charger.

The ammonium sulfate particles studied in the current investigation are somewhat unique, however, in that the sulfate must be thermally dissociated to produce sulfuric acid prior to detection. Laboratory tests in which equal moles of liquid sulfuric acid and ammonium sulfate are applied directly to the wire show that the same amount of sulfuric acid can be detected about 2 orders of magnitude more sensitively than sulfuric acid produced from the dissociation of ammonium sulfate. Thus the demonstrated sensitivity of the instrument to ammonium sulfate aerosol may represent a lower limit when compared to sulfuric acid or organic compounds, which are more directly desorbed and ionized.

One possible application for this instrument is to study the chemical composition of freshly nucleated aerosols, such as those observed previously in Atlanta, GA, USA, where sub-10 nm aerosols were observed at concentrations of up to 300,000 cm\(^{-3}\) (Woo et al. 2001). Using the TDCIMS with a unipolar charger (Chen and Pui 1999) and high throughput nano-DMA (de Juan and Fernández de la Mora 1998), 4 nm particles can be collected and charged to a concentration of 5300 cm\(^{-3}\) at a flow rate of 15 slpm. At this rate, 2 \( \times 10^7 \) particles, or 20 pg of ammonium sulfate aerosol, can be collected in 15 s. This is over an order of magnitude greater than the demonstrated detection limit for ammonium sulfate aerosols. Although particle collection can take place in as little as 15 s, total sampling interval also includes the 2.5 min needed to clean the wire and to allow the wire to return to ambient temperature. Thus the time resolution for such a measurement would be ca. 3 min. Thus, even at the present level of development, fast sensitive measurements could be made of nanometer size particles in the atmosphere.

Several improvements are under way on this instrument, including a redesign of the air outlet of the precipitator to reduce turbulence at higher flow rates, which should increase its sensitivity still further by reducing background and increasing collection efficiency. This should enable us to measure the chemical composition of particles down or below 4 nm in diameter, as well as measuring trace compounds, such as organics, that may be present in the particles.

REFERENCES


