Chemical Characterization of Individual Microparticles Using an Ion Trap: Real-Time Chemical Analysis of Aerosol Particles*

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ABSTRACT

This paper describes initial experiments to perform laser ablation mass spectrometry in real time on airborne microparticles. The microparticles are sampled directly from the air by a particle inlet system into the vacuum chamber of a mass spectrometer. An incoming particle is detected as it passes through two CW laser beams and a pulsed laser is triggered to intercept the particle for laser ablation/ionization in the mass spectrometer. The initial studies have been made with an existing ion trap mass spectrometer with the particle sampling occurring at the center of the trap electrodes. The performance of the inlet system, particle detection, and preliminary results are described.

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This paper describes initial experiments to perform laser ablation mass spectrometry in real time on airborne microparticles. The microparticles are sampled directly from the air by a particle inlet system into the vacuum chamber of a mass spectrometer. An incoming particle is detected as it passes through two CW laser beams and a pulsed laser is triggered to intercept the particle for laser ablation/ionization in the mass spectrometer. The initial studies have been made with an existing ion trap mass spectrometer with the particle sampling occurring at the center of the trap electrodes. The performance of the inlet system, particle detection, and preliminary results are described.

1. INTRODUCTION

The goal of this project is to develop an analytical technique to chemically characterize individual aerosol particles in real time. The targeted species are typically airborne particles bearing SNM and other signature compounds related to the production of weapons of mass destruction. Particles are introduced by direct atmospheric sampling and analyzed by laser ablation/desorption mass spectrometry. While the particle inlet system and laser ablation ionization can be used for the analysis of either organic or inorganic species, organic substances are best characterized by tandem mass spectrometry because of the
high degree of fragmentation and the large number of compounds with similar masses. An ion trap mass spectrometer has been shown to be effective for these species. On the other hand, time-of-flight mass spectrometry is the method of choice for rare airborne particles containing actinide elements, where only a few in a large number of particles will be important. Therefore, we plan to develop the atmospheric particle interface to be compatible with either type of mass spectrometer and to explore the applications of both.

The effort for the past year has been a scoping study to explore the feasibility of the project and get a start on the particle inlet system. Since an ion trap mass spectrometer was already available, we decided to concentrate on an instrument based on this technology. In addition to the individual particle mass spectrometry, which has been developed under earlier projects, the work included the construction of a reliable source of particles of known size and composition, the atmospheric particle interface, and a method for particle detection and laser triggering so that laser sampling occurs at the proper place and time. Progress in these areas is described below.

With the system in its present configuration, we have been able to obtain both primary and MS/MS spectra of several fuel-reprocessing extractants that might be encountered in the airborne effluent of a nuclear facility. Detection limits appear to be well below 100 fg per particle. We have also been able to obtain qualitatively reproducible primary mass spectra of both positive and negative ions from individual airborne bacteria in real time.

2. EXPERIMENT

Two configurations of particle generator have been used. The first is based on a vibrating orifice liquid droplet generator that produces a stream of monodisperse droplets 10 to 50 um in diameter. Solid particles are obtained by drying an aqueous solution of either the desired substance or a salt plus traces of the analyte. The particles are carried by airflow through a drying tube to the entrance aperture of the spectrometer interface. We have consistently been able to produce uniform particles of controlled size from potassium nitrate solutions in this way. The second system uses a Collison nebulizer instead of the vibrating orifice. The droplets produced are less uniform in size but the apparatus is less sensitive to clogging up. This system is used when solid particles are to be aerosolized. Particles can be coated by another analyte that is added in solution.

A diagram of the apparatus is shown in Fig. 1. The right-hand side of the figure represents the particle generator and drying tube. The inlet system and mass spectrometer are shown on the left. The particle inlet system has been evolving from an initial configuration of a short capillary tube leading into a differentially-
pumped chamber, separated from the ion trap vacuum chamber by a skimmer. While the ion trap pressure was acceptable with this configuration, the direct gas flow along the trap axis interfered with ion storage. Use of a longer capillary reduced this problem and permitted ion storage and mass spectrometry but alignment was difficult. We are presently using two skimmers to reduce the air load and using the shorter capillary to increase particle throughput. The inlet system samples approximately 0.6 L of air per minute.

The initial tests of laser ablation mass spectrometry were made with a Quanta-Ray Nd-YAG laser, operating on the third harmonic, at a wavelength of 355 nm. The output pulse from this laser is delayed by about 200 us from the time of triggering the flash lamps. The particles were accelerated to nearly the speed of sound, 150-300 m s\(^{-1}\) by the pressure drop in the interface.\(^3\) It was therefore necessary to sense the particles at two positions, one at least 6 cm from the trap center. We are using light scattering from two CW laser beams above the trap to sense the particles. The beams were initially from 30-mW CW diode lasers mounted within the vacuum chamber and the scattered light is directed by lenses and optical fibers to two external photomultiplier tubes. Because of the difficulty of aligning the beams within the chamber, the two diode lasers have been replaced with 5-mW HeNe lasers outside the chamber. An electronic timing circuit triggers the laser flash lamps and Q-switch so that the pulse intercepts the particle at trap center.\(^4\) An excimer laser is now available that can be used at higher duty cycle than the 10-Hz Quanta-Ray laser. While this laser has no flash lamps, constraints on the Thyratron still require particle sensing at two positions.

A block diagram of the electronics circuits needed to control the ion trap is shown in Fig. 2. PMT 1 and PMT 2 are the photomultiplier tubes that sense the particle's passage through the two CW laser beams. The Count Up and Count Down circuits ensure that the time from the second beam to the trap center is proportional to the time between the two beams. The counters are driven by two different clock frequencies, set so that the excimer laser is triggered when the particle arrives at trap center. The ion trap control functions as if the trap were a mass selective detector for a gas chromatograph, running a cyclical scan consisting of the following segments:\(^2\) an ionization period in which an electron gun is gated on and the trap conditions are set to store ions of a predetermined mass range, a selection interval in which ions of a particular m/z are isolated, an interval for collision-induced dissociation (CID) in which the selected ions are fragmented, and a mass scan in which the ions are ejected from the trap and detected in ascending order of m/z. If only a primary mass spectrum is desired, the two central segments are omitted. Since we are using laser ablation to generate the ions, the electron gun has been removed from our setup. We use the onset of the electron gun gate signal to latch the processor within the electronics package in HALT mode until the excimer laser is triggered. Thus, the ion trap is in the ion storage condition at the time the ions are generated and the desired mass spectrum will be acquired. After the data are stored, the control electronics package starts a new scan and is halted to await the next particle.
Once the process is initiated, the system is free running, acquiring mass spectra of every particle that triggers the pulsed laser.

The computer software used to control the ion trap is the ICMS package developed by Yost et al.\textsuperscript{5} A complication to tandem mass spectrometry on individual particles, at least with laser ablation sampling, is that the number of ions varies markedly from particle to particle. The secular frequency for ions of a given m/z in turn is a function of the number of stored ions.\textsuperscript{6,7} For efficient CID, however, the tickling voltage applied between the endcaps of the trap should have the same frequency as the secular frequency of the selected m/z ions. Since the ion count can neither be predicted nor adjusted, the tickle frequency is modulated over a specified range by the control software. The software package also provides a more flexible means to calibrate the mass scan.

Samples of TBP and HDEHP obtained from the Radiochemical Engineering Development Center at ORNL were used without additional purification. A typical charge in the Collison nebulizer would be 0.1 ml of the organic sample dissolved in 50 ml of methanol with 0.5 g of the carrier particles, either nominally 3-um SiC emery particles or kaolin powder approximately 1 um in size.

Once the control electronics have been set up and started, the apparatus is free running, with a mass scan measured and stored whenever a particle triggers the excimer laser. The particle flow rate is usually adjusted for a detection rate of 3-5 particles s\textsuperscript{-1}. Many of the events do not produce spectra, however, presumably due to misses. A particle that triggers the excimer laser must pass through the confocal region while the 10 ns pulse is present for a successful event. The maximum throughput is limited by the time required to complete an ion trap cycle and store the spectrum, typically 100 ms.

To test the apparatus with airborne bioparticles, bacteria were aerosolized from an aqueous suspension with a collison nebulizer. The droplets were passed through the heated drying column and cold trap. Particles that did not enter the apparatus are collected by an exhaust system. Freeze-dried bacteria, Bacillus subtilis, were obtained from Sigma Chemical Co. For a typical run, 200 mg of bacteria were mixed with 50 mL of water and placed in the nebulizer.

3. RESULTS AND DISCUSSION

Mass spectra of negative ions formed by laser ablation of TBP on SiC particles are shown in Fig. 3. The upper spectrum, Fig. 3a, is the primary spectrum. The parent ion, FW = 266.36 does not appear in these measurements. We show in Fig. 3b the spectrum of the isolated ion, (M-C\textsubscript{4}H\textsubscript{9})\textsuperscript{-}, at m/z 209, without CID, and in Fig. 3c, the MS/MS spectrum after CID of this ion. The two additional peaks at m/z 153 and 79 correspond to loss of C\textsubscript{4}H\textsubscript{9} and further loss of C\textsubscript{4}H\textsubscript{9}OH to PO\textsubscript{3}\textsuperscript{-}, respectively.
Similar results were obtained with HDEHP on SiC except for this substance the (M-H)⁻ ion appears in the spectrum, m/z 321. In Fig. 4a, we show the primary mass spectrum, in Fig. 4b the isolation of m/z 321, and in Fig. 4c, the MS/MS spectrum. Now the two additional peaks in the MS/MS spectrum are for loss of C₈H₁₆ at m/z 209 and further loss of C₈H₁₇OH to PO₃⁻ at m/z 79. An estimate for the amount of extractant on a particle can be made if it is assumed that all of the substance added to the nebulizer solution is in solution at the time of nebulization and that each particle receives all of the substance from its droplet. Independent measurements with particles evaporated from solutions of urea in methanol give a mean droplet size from the nebulizer of approximately 4 μm. We estimate that there would be at most 1 pg of extractant per particle for either the TBP or HEDHP measurements.

To make particles that better approximate those that might be encountered in the environment, we substituted kaolin powder for the SiC. Kaolin is a hydrated aluminum silicate clay that yields a large number of negative ions under laser ablation. The primary mass spectrum of a kaolin particle is shown in Fig. 5a. When HDEHP is added to the nebulizer as before, the HDEHP ions, except perhaps for PO₃⁻ at m/z 79, are obscured by the large kaolin background, as shown in Fig. 5b. However, if m/z 321 is isolated and dissociated, the characteristic three lines of the HDEHP MS/MS spectrum are observed, Fig. 5c. We estimate, with the same assumptions as above, that there would again be less than 1 pg of HDEHP on the particles measured here.

Representative mass spectra of positive and negative ions from single cells of B. subtilis are shown in Figs. 6 and 7 respectively. The positive ion spectrum is qualitatively similar to one presented by Sinha et al.⁸ We expect to see some differences between the two results because of the different sampling methods employed. Also, the mass resolution of our spectrum is probably degraded because of the large number of ions stored in the ion trap. The strong line at m/z is probably due to acetamide, a prominent feature in pyrolysis mass spectra of bacteria.⁹ The anion spectrum in Fig. 2 is more distinct since fewer species yield negative ions. Ions of both signs are stored in the ion trap for each particle sampled so the space charge effects on mass resolution should be approximately the same for anion or cation detection. The two strong features at m/z 79 and 97 are attributed to PO₃⁻ and H₂PO₄⁻ respectively. Many of the other numbered lines in Fig. 2 can be identified as being due to head groups of phospholipids commonly found in bacterial membranes or fragments of these head groups. For example, m/z 140 and 180 are associated with phosphatidylcholine.¹⁰ The lines at m/z 227 and 241 have been observed in negative ion fast atom bombardment mass spectra of bacterial phospholipids.¹¹ Lines at m/z 110 and 127 are probably methyl and methoxy additions to phosphoric acid. The relative intensity of the observed features varies from particle to particle. It is unclear at this time how much of this variation is due to the sampling and how much to differences from cell to cell.
We have shown in this study that it is possible to obtain structural information about molecular species in airborne microparticles with tandem mass spectrometry and to obtain sufficient background reduction in the MS/MS process so that a minor constituent can be identified. It is also possible to obtain representative spectra of airborne bacteria, all in real time. Since the apparatus is free running, analyzing each incoming particle that successfully triggers the ablation laser, the system could be used as an unattended monitor for particles bearing a target substance. Changing to a different target could also be accomplished remotely since only the ion trap scan function need be changed to select a new parent ion. Finally, there have been several recent developments in ion trap methodology and hardware that could be applied to improve the present system. The present particle inlet system is suitable either for ion trap mass spectrometry of organic particles or time-of-flight mass spectrometry of inorganics. We are presently working to extend the sensitivity so that submicron particles can be reliably analyzed.

4. REFERENCES


5. ICMS Ion Trap Software Version 2.20.


5. FIGURE CAPTIONS

Fig. 1. Diagram of the experimental apparatus

Fig. 2. Block diagram of the electronics control circuit.

Fig. 3. MS/MS experiments with TBP on SiC particles, negative ions. a, Primary mass spectrum. b, Isolation of m/z 209. c, MS/MS of parent ion, m/z 209.

Fig. 4. MS/MS experiments with HDEHP on SiC particles, negative ions. a, Primary mass spectrum. b, Isolation of m/z 321. c, MS/MS of parent ion, m/z 321.

Fig. 5. Negative ion MS/MS of HDEHP on kaolin particles. a, Negative ion primary mass spectrum of a kaolin particle. b, Primary mass spectrum of HDEHP on kaolin. c, MS/MS of HDEHP on kaolin, parent ion m/z 321.

Fig. 6. Positive ion primary mass spectrum of a single cell of Bacillus subtilis.

Fig. 7. Negative ion primary mass spectrum of a single cell of Bacillus subtilis.
TPF on SIC MicroParticles
MS/MS OF HDEHP ON SiC MICROPARTICLES

HDEHP on SiC

HDEHP on SiC isolation of m/z 321

ms/ms of HDEHP on SiC m/z 321
TANDEM MASS SPECTROMETRY OF HDEHP ON KAOLIN

1. kaolin spectrum

2. kaolin + HDEHP spectrum

3. HDEHP + kaolin - ms/ms of 321 spectrum