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Tandem Mass Spectrometry of Individual Airborne Microparticles

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An apparatus for real-time MS/MS analysis of individual airborne microparticles by laser ablation in an ion trap is described. The performance has been demonstrated by the detection of tributyl phosphate and bis(2-ethylhexyl) phosphate on silicon carbide and kaolin microparticles.

There is growing recognition of the health risks associated with airborne particulate pollution. Some recent studies have correlated the health effects with the concentration of atmospheric particles.^{1,2} Although the collected particles were analyzed for the presence of several elements, no causative agents were identified. Since there is a wide variation in toxicity among particles from different sources, such studies would be even more valuable if the particles could be individually characterized as to chemical composition. Sometimes the particles themselves may not be present in harmful quantities, but their presence may serve as an analytical indicator. For example, some substances of abuse and explosives have very low vapor pressures³ so that their presence in the environment is mostly in the condensed phase, either neat or adsorbed on surfaces and particulates. Several groups have reported advances in the use of laser ablation mass spectrometry to characterize individual airborne particles in real time.^{4–12} In this paper, we show that it is also possible to perform real-time tandem mass spectrometry (MS/MS) on individual aerosol particles by laser ablation/desorption within an ion trap mass spectrometer. Such measurements are especially valuable when specific organic substances that are trace constituents must be identified.

For test cases, we have analyzed airborne particles bearing two different organic extractants that are used for radiochemical separations: tributyl phosphate (TBP) and bis(2-ethylhexyl)-phosphoric acid (HDEHP). These substances might be found in the aerosol effluent from nuclear fuel reprocessing facilities. The carrier particles were either silicon carbide or kaolin. Substances deposited on the surface of silicon carbide can be sampled by

laser ablation/desorption with very little background signal due to the silicon carbide itself, especially when negative ions are detected. Kaolin, on the other hand, has a high negative ion yield but was used because it is representative of mineral particles that might be encountered in the environment.

EXPERIMENTAL SECTION

The experimental apparatus, shown schematically in Figure 1, is similar to that described by Yang et al.¹³ with the following differences. Sample particles were generated by producing microdroplets from a suspension of the solid carrier particles in a solution of the desired organic sample in methanol. The droplets were formed in a Collison nebulizer¹⁴ driven by dry compressed air at a pressure of 0.7×10^5 Pa above ambient. The droplets were then dried in the heated column described in ref 13 and introduced into the particle inlet of the spectrometer. The inlet system for these experiments consisted of a 2-cm-long 0.5-mm i.d. capillary followed by 0.5-mm- and 0.25-mm-diameter skimmers. Approximately 0.6 L of air entered the inlet system per minute. The pulsed laser for sampling the particles was a XeCl excimer laser with a pulse energy of nominally 5 mJ at a wavelength of 308 nm. The method of triggering this laser so that particles are sampled in the trap center is due originally to Sinha⁴ but has been modified somewhat to accommodate the different triggering delay of the pulsed laser.^{9,13} Scattered light signals were generated when a particle passed through two parallel CW laser beams focused at the axis of the apparatus. The CW laser beams, from two 4-mW HeNe lasers, entered and exited the chamber through Brewster windows. The scattered light was transmitted by optical fibers to photomultiplier tubes outside the apparatus. The signals from these PMTs controlled a timing circuit that generated an appropriate trigger pulse that fired the excimer laser and started the electronic scan function of the ion trap mass spectrometer. With this setup, particles as small as 0.8 μm in diameter could be reliably detected.

The ion trap consisted of a set of quadrupole electrodes and the electronics package from a Finnigan MAT ion trap mass spectrometer.¹³ The electrodes were housed in a cubical chamber as shown in Figure 1. Holes 3 mm in diameter drilled in the ring electrode provided a path for the particles and excimer laser beam. Mass spectra of trapped ions were obtained by ramping the rf voltage on the ring electrode of the trap.¹⁵ Positive ions were detected by a Channeltron multiplier placed behind a hole in the center of an end cap electrode. Negative ions were detected indirectly by means of a conversion dynode near the Channeltron.¹⁶ The mass scan electronics were synchronized to the

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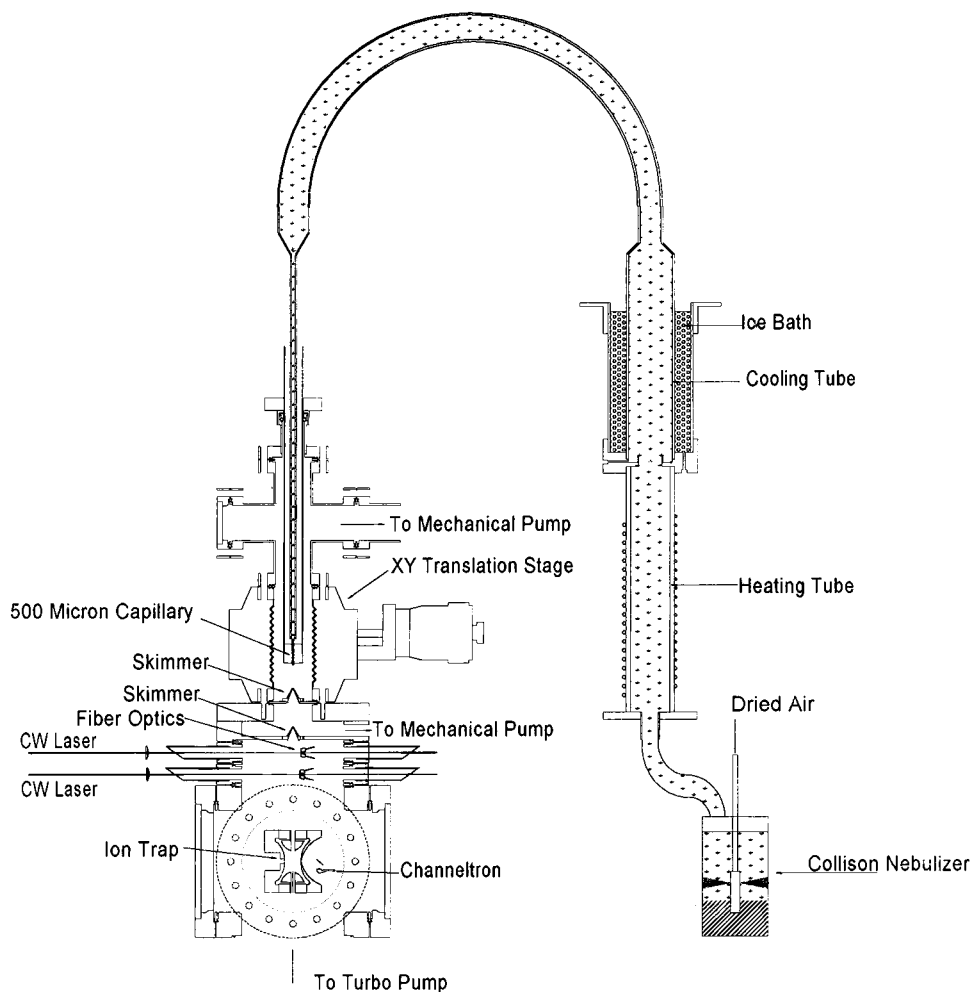


Figure 1. Diagram of the experimental apparatus. The XeCl laser pulses enter the ion trap through holes in the ring electrode in a direction normal to the page.

ablation pulse in the following way. The ion trap was operated in the "chromatograph" mode, in which the control circuit makes repeated scans of the trap voltages. A typical scan would consist of an ion collection period, a period during which the selected ions were fragmented by collision-induced dissociation (CID), followed by a mass scan of the product ions.¹⁷ The ionization gate signal from the original hardware was used to indicate when the scan function had started. At this time, the microprocessor controlling the trap was halted, the trap remaining in the ion collection mode until a particle was sampled, at which time the scan was resumed. The laser trigger was then disabled until a new scan had started. Primary mass spectra were obtained by eliminating the m/z selection and CID portions of the scan function.

The computer software used to control the ion trap was the ICMS package developed by Yost et al.¹⁸ 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.^{19,20} For efficient CID, however, the tickling voltage applied between the

end caps 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 was modulated over a specified range by the control software.

Samples of TBP and HDEHP obtained from the Radiochemical Engineering Development Center at Oak Ridge National Laboratory were used without additional purification. A typical charge in the Collision 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- μm SiC abrasive particles or kaolin powder $\sim 1 \mu\text{m}$ in size.

The size of the nebulized droplets before drying must be known to estimate the amount of solute that is deposited on the carrier particles. We nebulized a solution of urea in methanol and measured the size distribution of the dried urea particles at the entrance of the capillary with a calibrated particle impactor. From the size distribution of the dried urea particles and the solution concentration, we could calculate the droplet size distribution. This measurement indicated that droplet diameters ranged from 1.5 to 4.5 μm for most of the droplets. Thus, no more than one droplet in three would contain a kaolin particle

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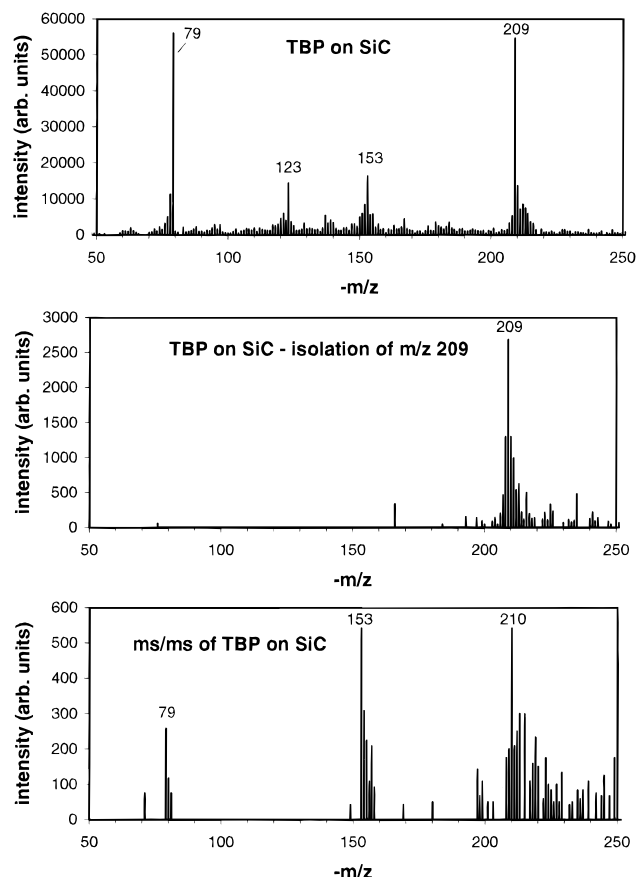


Figure 2. Negative ion MS/MS experiments with TBP on SiC particles: (a, top) Primary mass spectrum. (b, middle) Isolation of m/z 209. (c, bottom) MS/MS of parent ion, m/z 209. The mass labels above certain values of m/z were generated by the ICMS software and indicate prominent features with no regard for analytical significance.

and the ratio for the larger SiC particles would be much smaller, ~ 1 in 100. The size of a residual analyte particle with no particle substrate was less than $0.6 \mu\text{m}$, too small to be detected by our light scattering system. Collected particles with and without analyte were examined microscopically. The presence of analyte could not be discerned and there was no evidence of aggregation.

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 was usually adjusted for a detection rate of $1\text{--}3$ particles s^{-1} . Higher particle throughput did not appear to affect the storage or sampling, however. Laser triggering was inhibited during a mass analysis, and we did not observe perturbations when particles of this size passed through a stored ion cloud. Approximately one-third of the particles that triggered the laser would overlap spatially and temporally with the focused 10-ns excimer laser pulse and be sampled. The maximum measurement rate was limited by the time required to complete an ion trap cycle and store the spectrum, typically 100 ms.

RESULTS AND DISCUSSION

Mass spectra of negative ions formed by laser ablation of TBP on SiC particles are shown in Figure 2. Panel a shows the primary spectrum from a single TBP/SiC particle. The parent ion, $\text{FW} = 266$, does not appear in these measurements. The observed features are consistent with positive ions at m/z 211, 155, 125, and 81 observed in secondary ion mass spectrometry.^{21,22} We

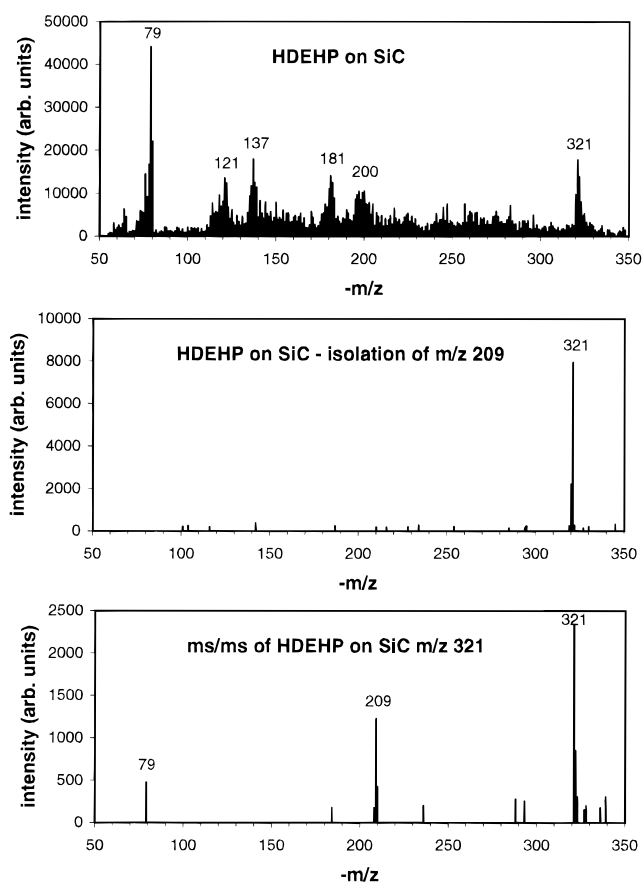


Figure 3. Negative ion MS/MS experiments with HDEHP on SiC particles: (a, top) Primary mass spectrum. (b, middle) Isolation of m/z 321. (c, bottom) MS/MS of parent ion, m/z 321.

show in Figure 2b the spectrum of the isolated ion, $(\text{M} - \text{C}_4\text{H}_9)^-$, at m/z 209, without CID, and in Figure 2c, the MS/MS spectrum after CID of this ion. The two additional ions at m/z 153 and 79 correspond to loss of C_4H_8 and further loss of $\text{C}_4\text{H}_9\text{OH}$ to PO_3^- , respectively. The ion at m/z 123 in the primary spectrum is attributed to $\text{C}_2\text{H}_4\text{PO}_4^-$ and is not evident in the CID spectrum. Positive ion tandem mass spectra of TBP that are consistent with our negative ion results have been measured by D'Agostino and Provost.^{23,24} These authors also observed that the positive ion, m/z 125, did not appear in the MS/MS spectra of the TBP fragments.²⁴

Similar results were obtained with HDEHP on SiC except that for this substance the $(\text{M} - \text{H})^-$ ion, m/z 321, appears in the spectrum. In Figure 3a, we show the primary mass spectrum, in Figure 3b the isolation of m/z 321, and in Figure 3c, the MS/MS spectrum. Now the two additional features in the MS/MS spectrum are for loss of C_8H_{16} at m/z 209 and further loss of $\text{C}_8\text{H}_{17}\text{OH}$ to PO_3^- 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. Based on our maximum measured

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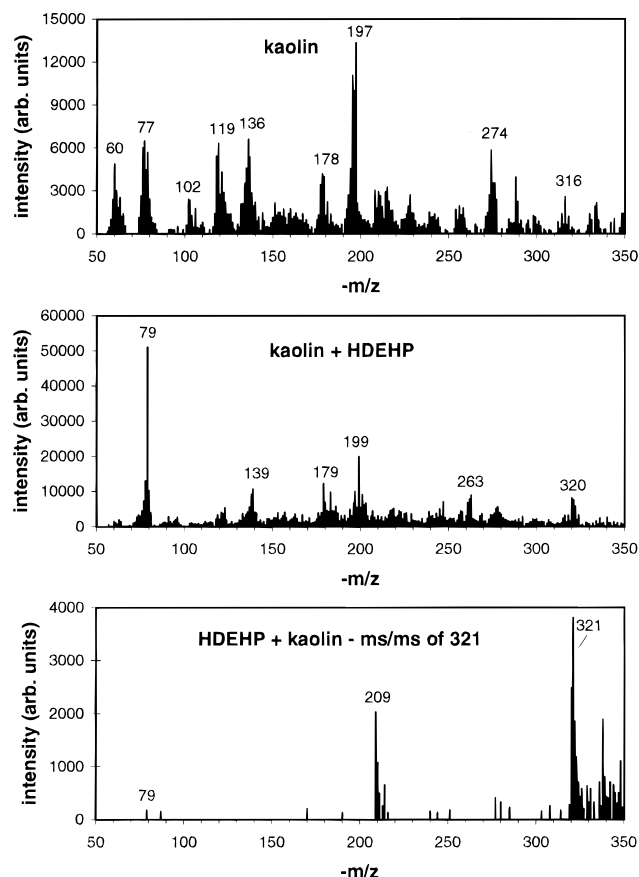


Figure 4. Negative ion MS/MS of HDEHP on kaolin particles: (a, top) Primary mass spectrum of a kaolin particle. (b, middle) Primary mass spectrum of HDEHP on kaolin. (c, bottom) MS/MS of HDEHP on kaolin, parent ion m/z 321.

droplet diameter of $4.5\ \mu\text{m}$ at the nebulizer, the largest amount of analyte on a given particle would be $\sim 100\ \text{fg}$.

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 Figure 4a. The negative ion mass spectrum shows many features that appear to be clusters of Al, Si, O, and H. When HDEHP is added to the nebulizer as before, the resulting spectrum is qualitatively similar (Figure 4b). Because of the considerable overlap between the spectra of HDEHP and kaolin, we could not say with assurance that HDEHP was present. However, when m/z 321 is isolated and collisionally dissociated, the three characteristic ions of the HDEHP MS/MS spectrum are observed, as shown in Figure 4c, confirming the presence of HDEHP. We estimate, with the same assumptions as above, that there would be less than $100\ \text{fg}$ of HDEHP on the particles measured here.

To test the sensitivity of the apparatus, we measured the primary mass spectra of HDEHP on SiC particles with reduced concentrations of the extractant in methanol in the nebulizer. In Figure 5, we show the average of 63 single-particle mass spectra with a 100-fold dilution, corresponding to a maximum of $1\ \text{fg}$ per

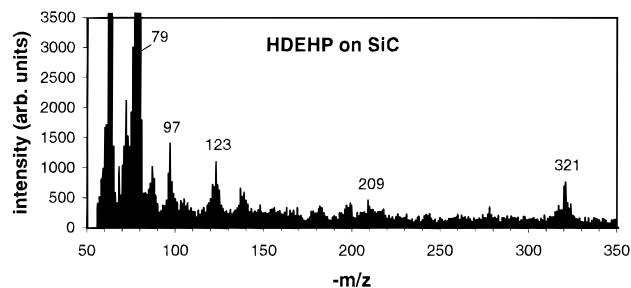


Figure 5. Primary negative ion mass spectrum of HDEHP on SiC, average of 63 single-particle measurements, with a sample loading of less than $1\ \text{fg}$ per particle.

particle, again with the assumption that the analyte is totally solvated before drying. HDEHP mass lines can be readily identified. More sensitive detection might be obtained with selective ionization through resonant excitation that might also reduce fragmentation, and with selective ejection of background ions that reduce the effective dynamic range of the ion trap. While $1\ \text{fg}$ is small in an absolute sense, it is still substantial in terms of the average mass of the carrier particles, $\sim 50\ \text{pg}$ for the SiC particles and $1\ \text{pg}$ for the kaolin particles. Accordingly, we would expect that these single-particle measurements would be more effective in detecting substances that are present as major impurities in some of the measured particles but might be found in very low concentrations in a bulk particle measurement.

We have shown in this study that it is possible to obtain structural information about molecular species in individual airborne microparticles with tandem mass spectrometry and to obtain sufficient background reduction in the MS/MS process so that molecular constituents can be identified. Also, the controlled conditions of CID of the mass-selected ions yield simple spectra that are easier to interpret than the primary laser ablation mass spectra that are complicated by the laser-particle-ion interactions during sampling and ionization. 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 would need to 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.^{25–28} We are presently working to extend the sensitivity so that submicrometer particles can be reliably analyzed.

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