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Detection of Chemical Warfare-Related Species on Complex Aerosol Particles Deposited on Surfaces Using an Ion Trap-Based Aerosol Mass Spectrometer

William A. Harris, Peter T. A. Reilly,* and William B. Whitten

Oak Ridge National Laboratory, P.O. Box 2008, MS6142, Oak Ridge, Tennessee 37831

A new type of aerosol mass spectrometer was developed by minimal modification of an existing commercial ion trap to analyze the semivolatile components of aerosols in real time. An aerodynamic lens-based inlet system created a well-collimated particle beam that impacted into the heated ionization volume of the commercial ion trap mass spectrometer. The semivolatile components of the aerosols were thermally vaporized and ionized by electron impact or chemical ionization in the source. The nascent ions were extracted and injected into the ion trap for mass analysis. The utility of this instrument was demonstrated by identifying semivolatile analytes in complex aerosols. This study is part of an ongoing effort to develop methods for identifying chemical species related to CW agent exposure. Our efforts focused on detection of CW-related species doped on omnipresent aerosols such as house dust particles vacuumed from various surfaces found in any office building. The doped aerosols were sampled directly into the inlet of our mass spectrometer from the vacuumed particle stream. The semivolatile analytes were deposited on house dust and identified by positive ion chemical ionization mass spectrometry up to 2.5 h after deposition. Our results suggest that the observed semivolatile species may have been chemisorbed on some of the particle surfaces in submonolayer concentrations and may remain hours after deposition. This research suggests that identification of trace CW agent-related species should be feasible by this technique.

There has been a tremendous amount of interest in real-time analysis of airborne particles. Mass spectrometry has been used for more than a decade for real-time analysis of aerosols.[1−9] The ultimate goal of aerosol mass spectrometry is real-time comprehensive quantitative analysis. One of the greatest barriers to this goal is a matrix effect that results from charge transfer that occurs as the particles are vaporized.[10] A solution to this problem is the separation of the vaporization and ionization processes. To date, the most successful methods used for quantitative molecular component analysis by aerosol mass spectrometry involve separate steps for vaporization and ionization.[7,11−13] One possible procedure for comprehensive analysis is thermal vaporization of the particles followed by gas-phase ionization to avoid the charge-transfer matrix effect that severely limits the applicability of the laser ablation/ionization mass spectrometry technique.

Most of the current research involving thermal desorption of particles followed by electron impact ionization utilizes either a quadrupole or time-of-flight mass analyzer.[6,9] Both have been successfully deployed in field campaigns and have demonstrated quantitative analysis of atmospheric particles. However, other mass analyzers may offer additional advantages. In particular, ion trap mass spectrometers are notably compact, inexpensive, and versatile. The ability to accommodate other methods of ionization such as chemical ionization (CI) and glow discharge ionization as well as perform tandem mass spectrometry (MS/MS) sets this platform apart. For example, chemical ionization can be used to reduce an interfering background and mitigate fragmentation. MS/MS can then be used to select and isolate an analyte from an intense background of ions for fragmentation and mass analysis. Here we describe a new instrument that has been developed by minimal adaptation of a commercial ion trap mass spectrometer for real-time analysis of semivolatile components of aerosols. The instrument was demonstrated by the identification of semivolatile analytes doped onto omnipresent substrate particles

* Corresponding author. Phone: 865-574-4919. E-mail: ReillyPT@ornl.gov.

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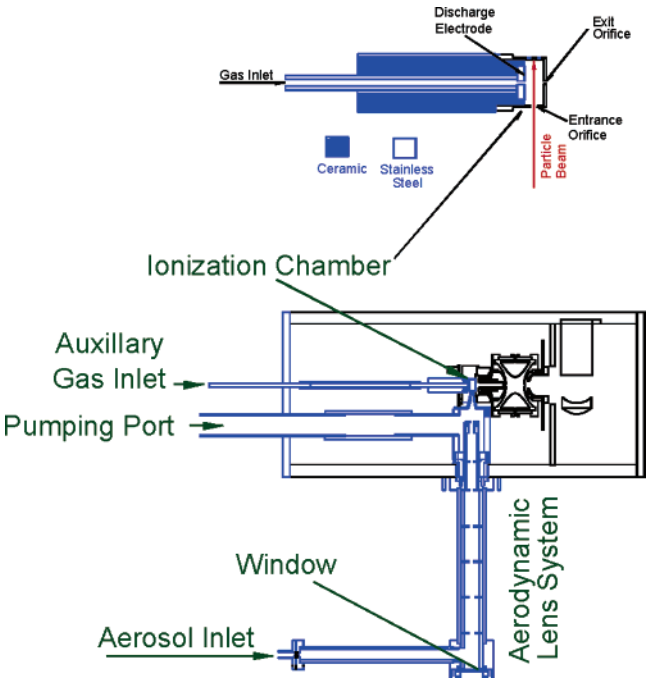

Figure 1. Cross-sectional drawing of the main vacuum chamber of the commercial ion trap (PolarisQ, ThermoFinnigan) with the modifications used to adapt it for use as an aerosol mass spectrometer. The figure includes an exploded view of the modifications made to the ionization volume.

such as house dust and soil. This work is part of an ongoing effort to develop methods for identifying chemical species related to chemical warfare (CW) agent exposure for the U.S. Department of Homeland Security.

EXPERIMENTAL SECTION

Instrument Modification:. Our instrument was produced by modifying a commercial ion trap mass spectrometer (PolarisQ, ThermoFinnigan, Austin, TX) originally designed as a mass analyzer for a gas chromatograph. A cross-sectional schematic of the instrument is shown in Figure 1. The original GC inlet was replaced with an aerodynamic lens-based inlet[14,15] designed to bolt in place without machining the main vacuum chamber. The aerodynamic lens system was pumped with a 70 L/s turbodrag pump (BOC Edwards) through a pumping port in the flange on the left of the diagram (Figure 1). The pumping port flange replaced a nominally blank flange that, in some models, was used for solid sample introduction and replacement/removal of the ion volume while the instrument remained at vacuum. This flange also incorporated an auxiliary gas inlet for introduction of gas for calibration or chemical ionization into the ionization chamber of the instrument. The ionization chamber was modified as to accommodate the gas inlet. The ionization source could be heated to 300 °C using the original commercial setup. A picture of the main chamber of the modified instrument is shown in Figure 2. Conversion of the off-the-shelf commercial ion trap mass spectrometer for aerosol analysis can be accomplished in less than 1 h. No software modification was necessary.

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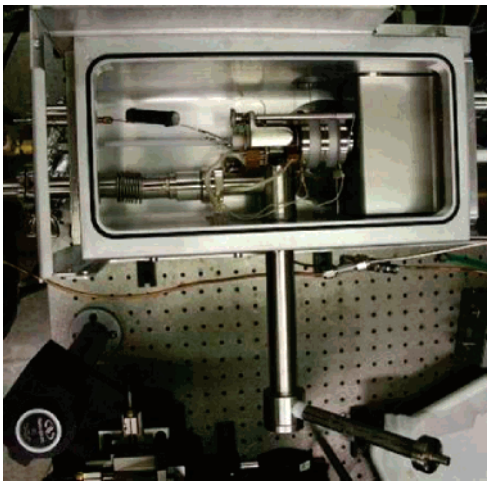

Figure 2. Top view of the instrument modifications used to convert the instrument for real-time aerosol analysis.

Analyte Particle Generation on Surfaces. The NIST standard reference material, Montana Soil, SRM 2710, and Standard House Dust (Greer Labs, Lenoir, NC) were used as substrates for analyte deposition. These particles were deposited on various surfaces that would be found in any office building. The procedure for substrate particle deposition on surfaces was as follows. The substrate particles were mixed with water. The resultant slurry was aerosolized with a collison nebulizer and dried by passing the wet aerosol through a heated tube and then a cooled tube to evaporate and condense the solvent. The emerging aerosol stream was then directed at the various surfaces for deposition by impaction. Deposition of the aerosols onto the various surfaces was not quantified. The surfaces used in this study were painted wallboard, glass, carpet, fabric and galvanized ductwork.

The substrate particles were doped with analyte after they were deposited on the surfaces. The analytes used in this study were trimethyl phosphite (TMP), trimethyl phosphate (TMPO), *N*,*N*-diethylaniline (DEA), dimethyl methyl phosphonate (DMMP), methylphosphonic acid (MPA), diisopropyl methyl phosphonate (DIMP) and tributylamine (TBA). Methanol solutions containing the analyte were deposited by pipet onto the "dusted" surface over approximately a 1-cm^2 area. The solvent rapidly evaporated and the analyte-doped particles were left to equilibrate for a measured amount of time before the particles were vacuumed from the surface through a 6-m tube. The inlet of the mass spectrometer sampled the vacuumed particle stream at 90° through a tee. Only a small fraction of the particles on the surface were sampled into the mass spectrometer inlet for analysis. Pure guanine particles were also generated by nebulizing a solution of guanine (1:1 methanol and water) and drying the particles in the manner indicated above. The guanine particles were sampled directly from the dried aerosol stream for the initial measurements. Methane was used as the chemical ionization agent in all CI measurements.

RESULTS AND DISCUSSION

The response of our instrument was first checked with a model aerosol of the nucleic acid, guanine. The guanine aerosol was produced using a collison nebulizer. A small portion of the resulting dried aerosol was admitted directly into the inlet of our mass spectrometer for analysis. The aerodynamic lens-based inlet

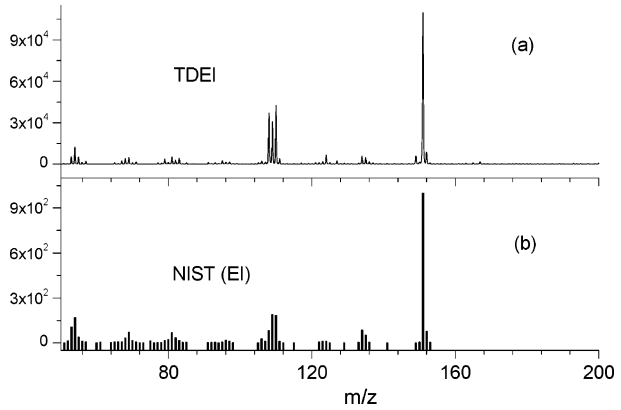

Figure 3. (a) Thermal desorption electron impact ionization spectrum of a laboratory-generated aerosol of guanine sampled from the air into the inlet of the mass spectrometer. Particles were impacted into the heated (300 °C) ionization chamber where they thermally desorbed and were subsequently ionized by electron impact. Ions were then extracted and injected into the ion trap for mass analysis. (b) EI spectrum of guanine from the NIST database.

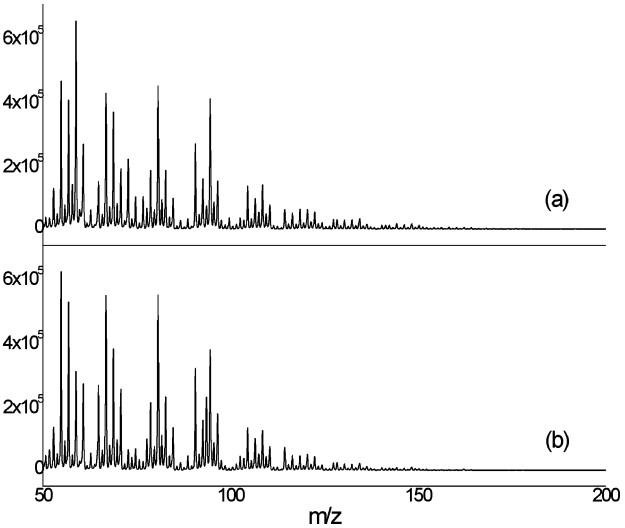

Figure 4. (a) Averaged thermal desorption electron impact mass spectrum of aerosolized Montana Soil (NIST SRM 2710). (b) The averaged thermal desorption electron impact mass spectrum of aerosolized Montana Soil (NIST SRM 2710) doped with 1 ppth tributylamine. The ionization chamber temperature was 300 °C. No discernible difference between these spectra was evident.

system creates a well-collimated particle beam in vacuum that can easily be separated from the carrier gas of the aerosol using differential pumping. The focused particle beam was impacted into the ion volume of the ion trap mass spectrometer where it was thermally desorbed at 300 °C and then ionized by electron impact. The resulting thermal desorption electron impact (TDEI) spectrum from the guanine aerosol is shown in top panel of Figure 3. For comparison we have shown the NIST EI spectrum of guanine in the bottom panel of the figure. Delivering the analyte as an aerosol yields a spectrum similar to that produced by NIST using standard EI MS methods.

The real test of our system is, of course, complex aerosols. In Figure 4a, we show the mass spectrum of Montana Soil (NIST SRM 2710). The aerosol was created by nebulizing a slurry of the soil. A portion of the resulting aerosol was then admitted into the inlet, collimated, and impacted into the ion volume at 300 °C.

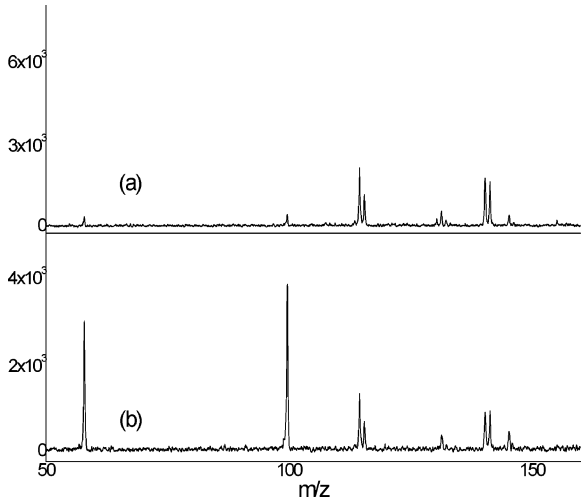

Figure 5. (a) Averaged thermal desorption electron impact tandem mass spectrum of aerosolized Montana Soil (NIST SRM 2710). (b) The averaged thermal desorption electron impact tandem mass spectrum of aerosolized Montana Soil (NIST SRM 2710) doped with 1 ppth tributylamine. The ionization chamber temperature was 300 °C; *m*/*z* 142 was isolated and subjected to collision-induced dissociation. The presence of tributylamine is indicated by the strong presence of ions at *m*/*z* 100 and 58.

The ion distribution results from the vaporization of the semivolatile components of the soil aerosol. It yields a congested spectrum because of the large number of organic components.

We began this research to determine if a particular component of a complex aerosol could be picked out and identified. In particular, we wanted to identify certain semivolatile species that might be associated with chemical agent aerosols to identify the process used to produce the agent. To initially test this concept, we added 1 ppth TBA (vapor pressure, 0.70 mmHg at 25 °C) to the Montana soil. The resulting spectrum of the soil and the tributylamine is shown in Figure 4b. Cursory comparison of the soil spectra shows no evidence of tributylamine even at the most prominent TBA ion, m/z 142. However, if we use the tandem mass spectrometry capability of the ion trap to isolate and fragment the m/z 142 ions, evidence of the addition of tributylamine becomes clear by the presence of fragment ions at m/z 100 and 58 in the tandem mass spectra in Figure 5. A small amount of the fragment ions at m/z 100 and 58 is noticeable in the blank. This was due to cross contamination of the tubing used to aerosolize and transport the particles from the surface that occurred during previous runs. The spectra in Figure 5 are the averages of 225 (top) and 162 (bottom) scans. It is likely that some of the particles that deposited on the tube walls got reentrained into the flow to be sampled during a blank run. This is a constant concern when sampling an aerosol through a tube, but it is easily recognizable by the large difference in the averages and by observing strong analyte signals occasionally among the blank spectra.

Chemical warfare agents are delivered as gases or aerosols. Eventually they deposit on surfaces. Existing environmental aerosols are efficient collectors that yield relatively large concentrations of the agents and their constituents relative to the mass of the substrate. House dust is a ubiquitous aerosol that exists in any building and can be found on virtually any surface. It therefore presents a standard surface for looking for the species that may identify the process used to make the agent. To test this concept,

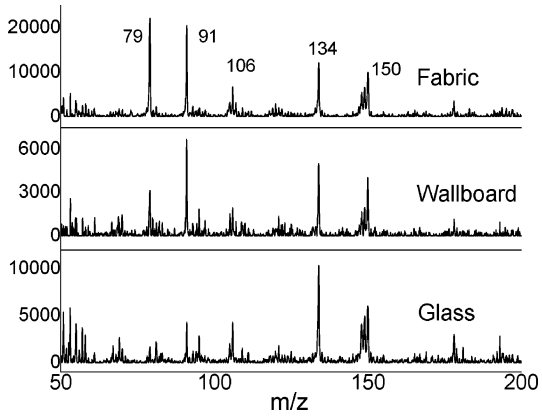

Figure 6. A 500-ng sample of diethylaniline in methanol deposited on (a) fabric, (b) painted wallboard, and (c) glass surfaces that have nebulized standard house dust impacted on their surfaces. The thermal desorption positive ion chemical ionization spectra were obtained by directly sampling the dust particle stream vacuumed from the various surfaces. These results suggest that the surfaces do not significantly affect the deposition onto the dust particles.

a standard house dust was aerosolized and deposited on various surfaces typical of those that might be found in any office building. A 500-ng sample of DEA in methanol was deposited by pipet onto 1 cm^2 of the "dusted" surface. The solvent was allowed to dry for ~2 min. The dust, containing some fraction of the deposited DEA, was then vacuumed off of the various surfaces and a portion of the vacuumed aerosol was sampled into the inlet of our mass spectrometer. Positive ion chemical ionization (PICI) spectra of DEA thermally desorbed from the dust particles sampled from fabric, painted wall board, and glass are shown in Figure 6. Comparison of the spectra obtained from the various surfaces show little variability, suggesting that the surface from which the dust particles are sampled does not affect absorption onto the dust particles.

House dust is extremely heterogeneous. Consequently, the different component particles in the aerosol should exhibit a range of affinities for various analytes. The heterogeneity of the material may make it an ideal substrate for detecting a large variety of chemical species. Some portion of the particles in house dust will likely bind the analyte more strongly than others. Stronger binding of the semivolatile analytes means that these compounds should linger and enable detection for longer periods of time. Measurements were made as a function of time between deposition and analysis to determine the feasibility of detecting semivolatile analytes long after the chemical agent was cleared from the room. A 50-μg sample of TMPO in methanol was deposited on a 1-cm^2 area of the dusted glass surface. Figure 7 presents the background-subtracted average of ~30 spectra of TMPO thermally desorbed from dust particles 15, 30, and 60 min after analyte deposition. After the solvent evaporates, evaporative loss of TMPO is relatively slow because the vapor pressure of TMPO is 0.85 mmHg at 25 °C. Figure 8 shows that the intensity of the TMPO ions relative to the dust ions make them easily observed even 2.5 h after deposition. This suggests that the TMPO may be chemically absorbed on some of the dust particle surfaces. This notion is supported by the total TMPO ion intensity versus scan number (top panel, Figure 8) observed as the vacuum hose is rastered across the dust-covered glass surface. Each point in the intensity

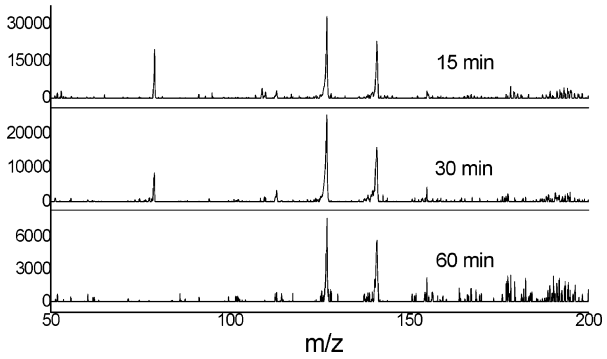

Figure 7. A 50-μg sample of TMPO in methanol deposited by pipet on a glass surface that had nebulized standard house dust impacted on the surface. The background-subtracted averaged thermal desorption positive ion chemical ionization spectra were obtained by directly sampling the dust particle stream vacuumed from the glass surface as a function of time (15, 30, and 60 min) after deposition of the semivolatile analyte solution.

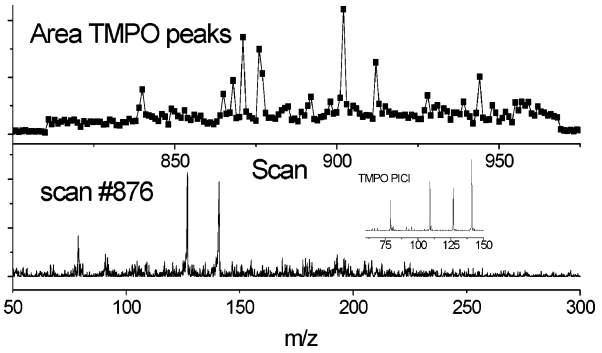

Figure 8. A 50-μg sample of TMPO in methanol deposited by pipet on a glass surface that had nebulized standard house dust impacted on the surface. (Top) The total TMPO analyte ion intensity in each individual mass spectrum plotted as a function of spectrum number as the TMPO-doped dust particles were vacuumed from the surface. (Bottom) Background subtracted TDPICI spectrum 876 of TMPO. (Inset) averaged PICI spectrum of TMPO.

scan represents the summed intensity of the TMPO ions in a separate mass spectrum (average of 10) taken approximately every 2 s. The first points in the intensity scan represent the mass spectra from background air. The first rise in the baseline represents the initiation of vacuum sampling from the surface. Next, sharp rises and falls of the TMPO ion intensity suggest that the analyte-containing particles are entering the heated ionization chamber in discrete bursts and that only a few analyte-containing particles enter the chamber at a given time. In the average of all of the spectra of the particles vacuumed off the surface, the analyte peaks would be difficult to discern from the dust background. If the analyte were evenly distributed over the ensemble of dust particles distributed on the surface, as it would be if it were primarily physisorbed, the total analyte ion intensity would have been more uniform and not present as spikes of analyte-containing particles.

The discrete nature of the intensity change gives an indication of the sensitivity of the technique. The aerodynamic lens system is designed to focus particles below 3.5 μm in diameter. Particles in the 1-μm size range have masses of the order of 1 pg. Chemisorbed analyte suggests monolayer coverage or less and further suggests that the dust particle substrate represents the majority of the particle mass sampled into the instrument. If the

signal spikes are due to roughly single analyte-containing particles, then our actual analyte sensitivity is less than a picogram.

Similar results were observed for the other analytes, TMP, DEA, DMMP, MPA, DIMP, and TBA. However, the technique appeared to be less sensitive for some of the analytes. For example, greater than 50 μg of methylphosphonic acid had to be deposited on the surface in solution to be observed. Loss of sensitivity may result for a variety of reasons. One possibility may be the deposition method. Some analytes could rapidly evaporate due to analyte volatility and avoid mass analysis. Conversely, the analyte could remain adsorbed on the particles even at the thermal desorption temperature of 300 °C. Another possibility is decomposition of the analyte with the decomposition product ions masked by the presence of dust or background-related ions. Further experiments are required to investigate sensitivity losses and procedures for avoiding them.

Future experiments will involve gas-phase deposition of semivolatile analytes onto substrate particles to yield a more realistic simulation of deposition from an event and provide a better measure of sensitivity. Small exposures of analyte deposited on the dust particles by adsorption from the gas phase are likely to be observable many hours or perhaps even days after exposure if they are chemically bound (chemisorbed) to the particles as our results suggest. These future experiments will provide a better understanding of the limitations of the technique. Our initial measurements indicate that CW-related species of the various synthetic processes used to produce chemical agents may be discerned with this technique. Future experiments will also include using a differential mobility analyzer to introduce monodisperse aerosols into the inlet of our mass spectrometer for size-selected aerosol analysis.

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