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Laser Desorption/in Situ Chemical Ionization Aerosol Mass Spectrometry for Monitoring Tributyl Phosphate on the Surface of Environmental Particles

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The possibility of using real-time aerosol mass spectrometry (RTAMS) for the detection of surface-adsorbed tributyl phosphate (TBP) as an alkali metal adduct has been investigated. Environmental particles contain variable amounts of easily ionizable alkali metals. During laser desorption of surface-adsorbed TBP molecules, Na$^+$ and K$^+$ ions are generated by the interaction of the laser radiation with the particle's material. The alkali metal ions serve as in situ chemical ionization reagents of the neutral analyte molecules. The effect of laser fluence on the signal intensities of the potassium ion and cationized TBP was also studied. The best performance of the instrument was observed with laser fluences that produce high abundances of K$^+$ but low abundances of ions from the particle's bulk material. The relatively low laser fluence, necessary to produce potassium ions, prevents the excessive fragmentation of the analyte. The instrument is capable of real-time monitoring of submonolayer coverage of TBP on the surface of micron-sized particles.

There has been continuous interest in the development of analytical methods for real-time monitoring of environmental pollutants. Semivolatile organic compounds have a tendency to adsorb onto the surface of aerosol particles of respirable sizes and pose potential health hazards. Conventional methods used for the analysis of organic compounds that are present on the surface of aerosol particles are based on particle collection followed by extraction and chromatographic analysis of the extracted organic species.[1,2] These methods require large quantities of samples and long analysis times.

In recent years, several research groups have reported real-time chemical analysis of aerosols.[3−12] Airborne particles are directly aspirated into a vacuum chamber where they are ablated and ionized by a laser pulse, followed by mass spectrometric detection of the ions. Several instruments are capable of providing size, number density, and composition information about the aerosols. The relatively high laser fluence necessary to ionize analyte molecules present on the surface of aerosol particles produces a high abundance of ions from the bulk material that can obscure weak signals from surface-localized species. Charge-transfer processes specific to the matrix can also alter the analytical results.[13] Single-step laser desorption/ionization aerosol mass spectrometry is mainly suitable for the characterization of the chemical composition of the particles' bulk material. Two-step laser desorption ionization has been coupled with aerosol mass spectrometry to reduce fragmentation of organic species[14] or to reduce space charge effects in the ion source of the mass spectrometer,[15] but none of these experiments were specifically designed to analyze molecular adsorbates on particles. We recently reported the surface analysis of particles by using two-step laser desorption/ionization real-time aerosol mass spectrometry (L2RTAMS).[16] The instrument is capable of real-time monitoring of polycyclic aromatic hydrocarbons (PAHs) adsorbed onto the surface of airborne particles without significant time delay between analysis and environmentally significant events. The disadvantage of L2RTAMS is that it requires two lasers, which complicates the instrumentation. For this reason, another type of ionization source is more desirable. Electron impact (EI) or conventional chemical ionization (CI) is not capable of producing significant amounts of analyte ions before the laser-desorbed neutral molecules leave the volume of the ionization source. Metal ions have been employed

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for several decades for chemical ionization of organic compounds and of molecules of biological interest.[17-20] Alkali metals have low ionization potentials, and ions can be produced by laser irradiation of the surface of different materials containing alkali metals. The formation of alkali cations during laser desorption has been observed even when alkali metals were present only as impurities.[18]

In this paper, we describe the detection of tributyl phosphate (TBP) present on the surface of aerosol particles by using aerosol mass spectrometry. TBP was chosen as the test analyte because it was widely used for the extraction of plutonium and uranium and it might be present in the aerosol effluents from some Department of Energy facilities. Another reason TBP could be of interest is that phosphate esters serve as simulants for chemical warfare agents.[21] Reilly and co-workers used aerosol mass spectrometry to detect TBP on the surface of silicon carbide and kaolin particles in the negative-ion mode.[11] The resulting mass spectra contained TBP fragment ion peaks along with ions from the bulk material. The molecular ion was not observed. Isolation of the highest mass fragment ion followed by MS/MS was necessary to confirm the identity of TBP. Recently, Gill and co-workers reported in situ chemical ionization of TBP adsorbed on the surface of silver-containing zeolites.[22] Resonant laser desorption produced silver ions and simultaneously vaporized TBP molecules. The silver ion adducts provided relative molecular mass information about the analyte.

In our experiment, we took advantage of the fact that environmental particles contain easily ionizable alkali metals. It has been observed that very low levels of alkali metals present as impurities are able to produce cationized analyte ions. Potassium and sodium ions produced by laser radiation served as in situ chemical ionization reagents of TBP.

EXPERIMENTAL SECTION

General Procedures. The instrumental setup has been presented elsewhere.[11-13] Briefly, airborne particles are aspirated into an ion trap mass spectrometer (Finnigan MAT, San Jose, CA) through a differentially pumped inlet (Figure 1). Two parallel argon ion laser beams intersect perpendicularly the path of the collimated aerosol beam in a vacuum chamber. Two photomultiplier tubes (PMTs), detect the scattering pulses produced by the particles. The electrical signals from the PMTs are processed and used for triggering of the mass spectrometer and an XeCl excimer laser (model AQX-150, MBP Technologies). When a particle arrives in the center of the ion trap, the laser fires, producing ions that are detected by the mass spectrometer. During this work, we used 0.2 and 1 J/cm² laser fluences.

The mass spectrometer was operated in the "chromatograph" mode, in which the instrument generates and stores repeated scans.[11] The stored spectra were sorted as a function of total ion current. Spectra with total ion current values below a certain
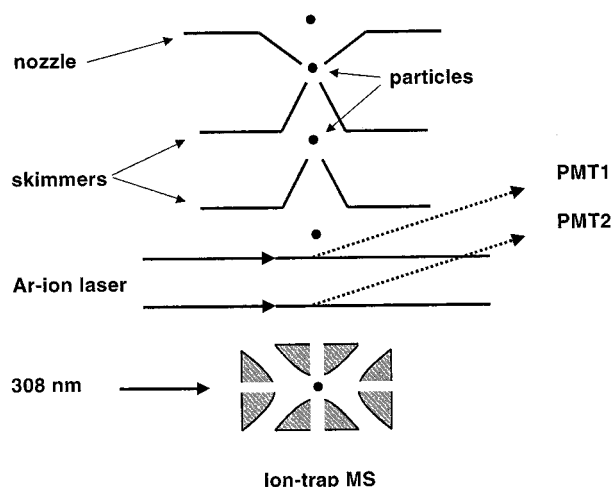

Figure 1. Schematic representation of the experimental setup.

threshold were considered "misses" and discarded. The retained spectra were further sorted and/or averaged.

Sample Preparation. Montana Soil from the National Institute of Standards and Technology (SRM 2710) and silicon carbide abrasive particles (Grit 600, Bhueler Ltd., Evanston, IL), coated with TBP (Eastman Kodak Co., Rochester, NY), were used as test samples. Initial experiments were performed using the coating procedure that has been previously described and evaluated by Reilly and co-workers.[11] Briefly, 0.5 g of particles was introduced into 50 mL of methanol (EM Science, Gibbstown, NJ) that contained 2 mg/mL tributyl phosphate. The suspension was nebulized with a Collison nebulizer. The aerosol passed through a drier, and the dried particles were carried to the inlet of the mass spectrometer. The aerosol generated by this procedure contained an estimated 100 fg of TBP on the surface of a single particle. Another coating procedure, which generated lower surface coverage, was also employed where 100 mg of particles was spiked with 100 μL of TBP stock solution. The stock solution contained 1 mg/mL TBP in acetone (EM Science, Gibbstown, NJ). The solvent was evaporated in air under a hood. The coated particles were mixed with 20 mL of deionized water, and the suspension was nebulized with a Collison nebulizer. TBP has low solubility in water, and one can assume that most of the tributyl phosphate molecules remained on the surface of the particles. The aerodynamic size distribution of Montana Soil ranged from 0.7 to 4.5 μm. By assuming 2 μm diameter spherical particles, we estimated the coverage achieved by this method to be 0.45 monolayer of TBP on Montana Soil. Dried powder introduction by dust generation with a magnetic stirrer was also used, but it was less practical with coated samples, because they had an increased tendency to stick to the wall of the container and to the wall of the transfer line. When the aerosol was properly dried, no significant difference in the mass spectrometric results could be observed between aerosol generation through nebulization from solution or dried powder introduction.

RESULTS AND DISCUSSION

The averaged positive-ion mass spectra of Montana Soil particles without and with TBP are presented in Figure 2. The particles were coated during nebulization from TBP containing methanol solution, as described in the sample preparation section.

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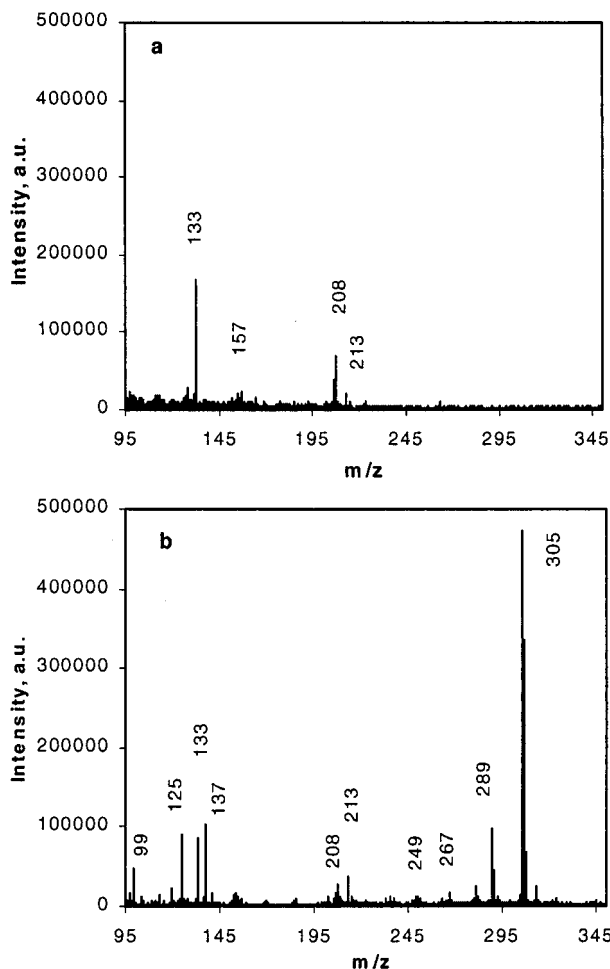
Figure 2. Averaged mass spectra of Montana Soil particles obtained using a laser fluence of 0.2 J/cm^2: (a) particles with no added TBP (175 spectra averaged); (b) individual particles coated with approximately 100 fg of TBP, which corresponds to multilayer surface coverage (272 spectra averaged).

Figure 3. Averaged mass spectra of Montana Soil particles with an estimated surface coverage of 0.5 monolayer TBP ($\sim$7 fg of TBP per particle): (a) 0.2 J/cm^2 laser fluence (334 spectra averaged); (b) 1 J/cm^2 laser fluence (815 spectra averaged).

The major peak from the analyte at m/z 305 corresponds to the potassium adduct [TBP + K]$^+$, and it appears in the region of the spectrum where the abundance of ions from the bulk material of the particles is low. The sodium adduct peak at m/z 289 has lower intensity, while the protonated TBP peak at m/z 267 is barely detectable. The spectrum also contains peaks corresponding to TBP fragment ions. The peak at m/z 99, which is the major peak in the EI mass spectrum of TBP, is due to the protonated phosphoric acid ion [H$_4$PO$_4$]$^+$ resulting from the loss of three butene molecules.[23] The m/z 125 fragment is the protonated vinyl phosphoric acid ion. A small peak at m/z 249 is due to [TBP − OH]$^+$, while the m/z 137 fragment ion is formed by further loss of two butene molecules.[24]

The high intensity of the alkali metal adduct ions originating from particles coated with approximately 100 fg of TBP suggested that submonolayer surface coverage could also be detected. Montana Soil particles with an estimated coverage of $\sim$0.5 monolayer of TBP were analyzed using two different laser fluences. Figure 3a shows the average of 301 individual spectra
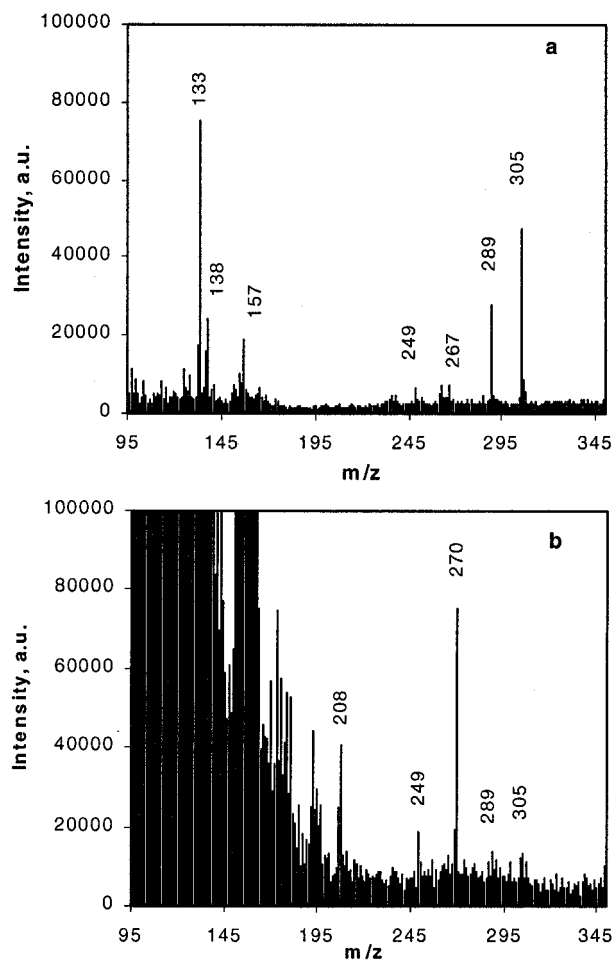
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obtained by using a 0.2 J/cm^2 laser fluence. The [TBP + K]$^+$ adduct ion could easily be detected. The m/z 305 peak is 22 times higher than the averaged background signal. The averaged background signal was determined off peak using 35 points in the region between m/z 310 and 334. Figure 3b contains the average of 815 spectra acquired with 1 J/cm^2 laser fluence. In the low-mass region, high laser fluence produced a high abundance of ions characteristic of the bulk composition of the particles.[13] Above m/z 200, the spectrum contains peaks from Pb$^+$ and UO$_2$$^+$ ions at m/z 208 and 270, respectively. The cationized TBP peaks have lower intensities, while the protonated analyte ion is not observable. The m/z 305 peak is only 2.6 times higher than the averaged background signal.

To obtain more information about the relationship between the production of alkali metal ions and cationized TBP ions, and the effect of laser fluence on the analyte signal, the spectra used in Figure 3 were grouped in bins as a function of the relative ion current (RIC). Table 1 contains the number of spectra and the RIC limits for each bin. The spectra within a bin were averaged, and the intensities of the K$^+$ and [TBP + K]$^+$ions were plotted in Figure 4. There is a relatively high fluctuation of RIC acquired from individual particles. We observed these fluctuations with particles of similar sizes and compositions. The variations are mainly due to fluctuations of the laser fluence that effectively

Table 1. Bin Numbers Corresponding to Different RIC Ranges

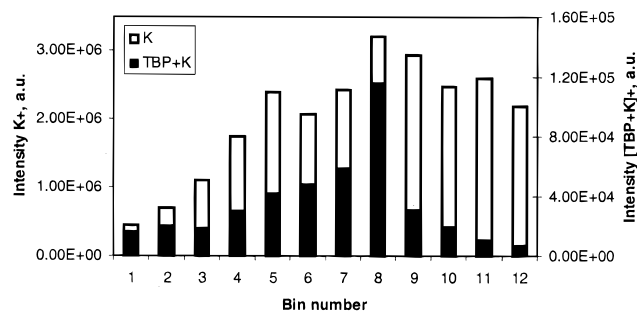| bin no.	no. of spectra per bin	RIC range
1	34	$10^6 - 1.25 \times 10^6$
2	43	$1.25 \times 10^6 - 1.75 \times 10^6$
3	38	$1.75 \times 10^6 - 2.5 \times 10^6$
4	44	$2.5 \times 10^6 - 3.5 \times 10^6$
5	34	$3.5 \times 10^6 - 5 \times 10^6$
6	34	$5 \times 10^6 - 8.5 \times 10^6$
7	35	$8.5 \times 10^6 - 1.05 \times 10^7$
8	38	$1.05 \times 10^7 - 1.8 \times 10^7$
9	173	$1.8 \times 10^7 - 3 \times 10^7$
10	240	$3 \times 10^7 - 5 \times 10^7$
11	135	$5 \times 10^7 - 7.5 \times 10^7$
12	68	$7.5 \times 10^7 - 10^8$

Figure 4. K^+ and $[TBP + K]^+$ signal intensities as a function of total ion current (see Table 1). White bars correspond to K^+ (left scale); black bars represent $[TBP + K]^+$ (right scale).

Figure 5. Mass spectra of Montana Soil particles covered with 0.5 monolayer of TBP obtained by averaging the spectra from (a) bin 1, (b) bin 8, and (c) bin 11.

interacts with the particles. Pulse-to-pulse fluctuation of the laser beam energy is one of the causes of the variations. Spatial inhomogeneity of the laser fluence, due to a Gaussian energy distribution, and "hot spots" in the beam also contribute to the observed signal variations. The particle's diameter is about 2 orders of magnitude smaller than the diameter of the focused laser radiation in the center of the ion trap. Jitter in the triggering signals and spatial spread of the particle beam superimposed on the spatial inhomogeneity of the laser energy density can cause variable laser fluences on the surface of the particles even when the total energies of the laser pulses are the same. It is not surprising that a relatively wide range of RIC values can be obtained with relatively constant total laser fluence. Therefore, one can expect that there is a correlation between total ion current and effective laser fluence on the surface of the particles. By sorting the data as a function of RIC, we can obtain information about the effect of laser fluence on the mass spectra. From Figure 4 one can see that, at low RIC values (bins 1−8), the intensity of $[TBP + K]^+$ increases with the increasing intensity of K^+. At high total ion currents (bins 9−12), the signal intensity of K^+ slightly decreases. The examination of the averaged mass spectra corresponding to the 12 bins (three spectra are shown in Figure 5) revealed that the signal intensity of other species present in the particles' bulk material increases with increasing total ion current. Potassium could be found in the spectra as adduct species. The averaged mass spectra from bins 1, 8, and 11 are presented in Figure 5. At low RIC values, the spectrum contains low-intensity adduct ion peaks (Figure 5a). The intensity of Cs^+ at m/z 133 is also very low. The spectrum in Figure 5b corresponds to bin 8, in which the highest signal intensity was obtained for both K^+
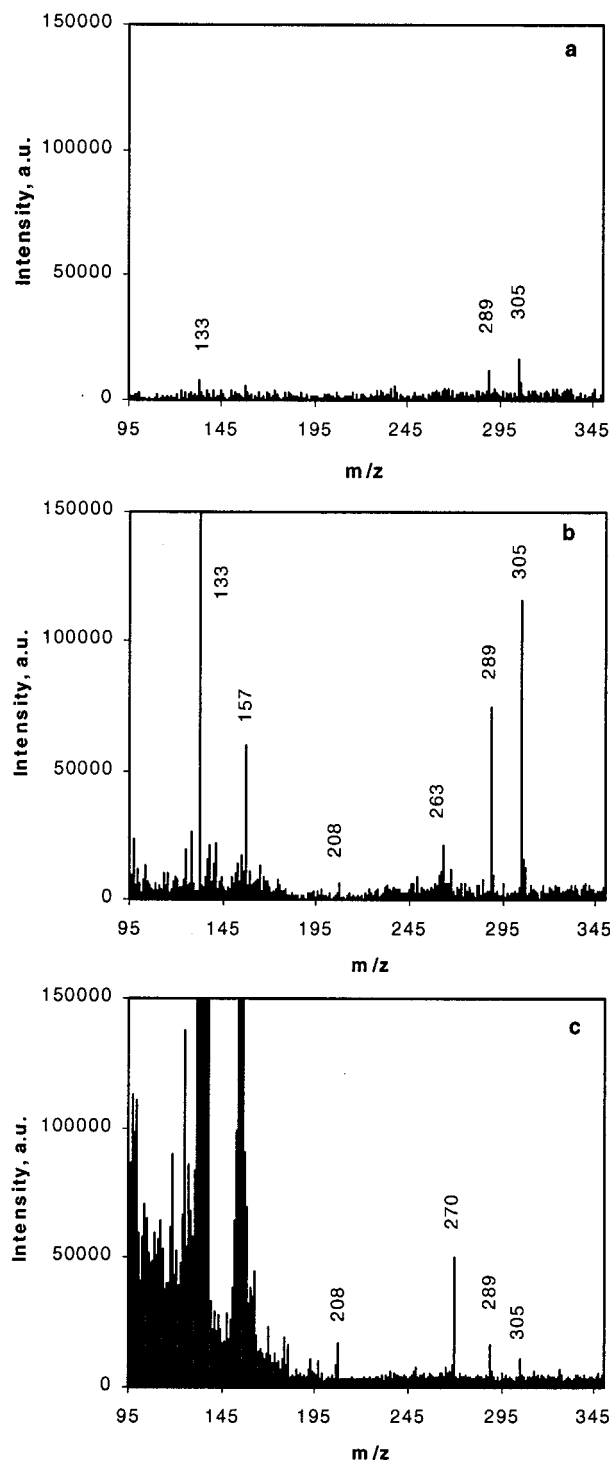
and $[TBP + K]^+$ ions. At high total ion currents, the cationized TBP peaks decrease and the background level below m/z 200 increases substantially (Figure 5c). At very high RICs the $[TBP + K]^+$ signal is not distinguishable from the background signal. The results suggest that there is an optimum range for the effective laser fluence that produces high signal intensities of cationized TBP ions. The applied laser fluence should be high enough to generate a high abundance of alkali metal ions but low enough to avoid extensive production of species from the bulk

material of the particles. The disappearance of the peak at m/z 305 could be the result of matrix effects occurring in the plume. Other factors should also be considered. High laser fluence can generate gas-phase molecules with high internal energies.[25] High internal energy can affect the cationization process of the analyte molecules. High laser fluence can also produce pronounced fragmentation of TBP. It is difficult to detect TBP fragment ions in the averaged mass spectra of Montana Soil at high RIC values because of the high background level in the spectrum where fragment ions are expected to appear.

The effect of high laser fluence on TBP decomposition was investigated using laser desorption/in situ chemical ionization aerosol mass spectrometry of SiC particles coated with TBP. The background level in the SiC mass spectrum is lower than the background level in the mass spectrum of the soil and allows the observation of TBP fragment ions. The amount of 1 mg of TBP/g deposited on the surface of silicon carbide particles was the same as the amount coated on Montana Soil particles. The surface coverage with TBP was higher on SiC than on Montana Soil because silicon carbide particles have higher densities and larger sizes. For nominally 3 μm diameter particles, the estimated coverage was slightly above one monolayer. The averaged positive-ion mass spectra of the coated SiC particles obtained at two different desorption laser fluences are presented in Figure 6. Both spectra contain adduct and fragment ions, but the relative intensities of the peaks are very different. At low fluence, the major peak originating from TBP is the potassium adduct ion. At high fluence the peak heights of adduct ions decrease, while the intensities of the fragment ions increase and the protonated vinyl phosphoric acid ion at m/z 125 becomes the major peak. The results clearly indicate that high laser fluence causes decomposition of the TBP molecules and suggest that the applied laser fluence should be carefully selected for the detection of cationized TBP. Our system exhibited good performance with laser fluences around 0.2 J/cm².

CONCLUSIONS

The applicability of laser desorption/in situ chemical ionization real-time aerosol mass spectrometry for monitoring the presence of TBP on the surface of environmental particles has been demonstrated. By employing relatively low laser fluence, we can detect submonolayer TBP coverage on the surface of micron-sized single particles. Voumard and co-workers used conventional L2MS for the detection of aniline on silica surfaces and reported the detection of molecular surface species at the 10^{-6} monolayer level.[26] The surface area from which aniline molecules were desorbed was at least 10^6 times greater than the surface area of the particles analyzed in our instrument. Therefore, the performance of RTAMS with laser desorption/in situ chemical ionization for the detection of surface-adsorbed TBP is comparable to the detection of surface adsorbates using conventional L2MS.

The fluctuation of the effective laser fluence is one of the factors that limit the performance in laser desorption/ionization aerosol mass spectrometry. The ion signal has a steep dependence on laser fluence in the region close to the ion production threshold. Homogeneous spatial distribution of the energy of the laser is
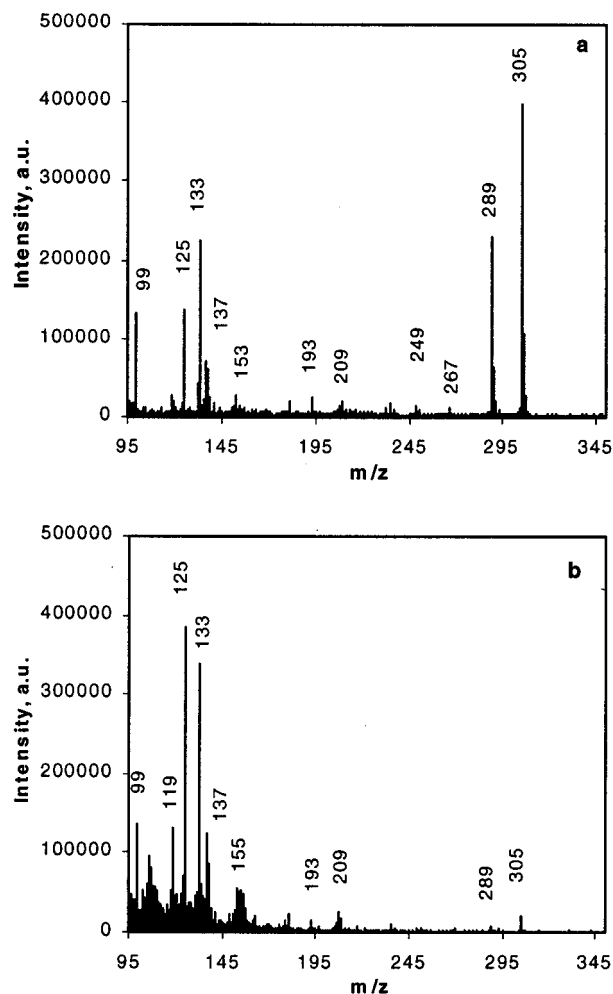

Figure 6. Mass spectra of SiC particles covered with approximately one monolayer of TBP acquired at two different laser fluences: (a) 0.2 J/cm² (284 spectra averaged); (b) 1 J/cm² (217 spectra averaged).

expected to reduce signal fluctuations. The performance of our system might be improved by using a "flat-top" laser profile.[27] A flat profile would allow us to ensure that the laser beam uniformly overlaps the particle beam, which could eliminate the signal variations due to laser–particle interactions in different spatial locations inside the laser beam.

The disadvantage of detecting TBP as an alkali metal adduct ion is that the MS/MS capabilities of our ion trap mass spectrometer cannot be exploited, because the charge of the dissociated ions is carried by the alkali metals, and no information about the organic compound can be obtained. On the other hand, the formation of adduct ions has the advantage that it shifts the m/z ratio of the pseudomolecular ion to higher values, where the background intensity is lower and few ions from the particles' bulk interfere with the detection of the analyte. On the basis of the results presented in this paper, one can conclude that laser desorption/in situ chemical ionization aerosol mass spectrometry is a promising technique for real-time monitoring of the surface of environmental particles. The method is especially suitable for the detection of molecular adsorbates that have a strong tendency to form alkali metal adducts.

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