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Modifications to an analytical mass spectrometer for the soft-landing experiment

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Abstract

Modifications to a hybrid geometry beam mass spectrometer are described that allow its use for soft-landing of ions onto a stainless steel surface intercepting the ion beam at the site of the intermediate detector. Initial success is documented through the presence of metal ions brought to the surface as part of a complex, metal-containing cluster ion. Further, organic cations have also been soft landed at the collector surface, and electrospray ionization (ESI) and ESI tandem mass spectrometry analysis of the surface wash solution confirm preservation of the original organic structure. Future directions for predictable surface density collection strategies are described. (Int J Mass Spectrom 182/183 (1999) 415–422) © 1999 Elsevier Science B.V.

Keywords: Soft landing; Hybrid mass spectrometer; LSIMS; ESI; Cluster ions

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1. Introduction

Controlled deposition of ionic and molecular species onto surfaces has been studied from perspectives as diverse as the physics of the soft-landing experiment, to the methods of preservation of the intact chemical structure of the ion placed on a chemically modified surface, through to the deposition of an intact virus onto a surface covered with glycerol [1–15]. Soft landing is defined as the collection of a specific ion of complex structure on a surface with preservation of that structure. Successful soft-landing experiments may lead to the creation of nanophase materials or chemically engineered surfaces of special properties or surfaces with special biological properties, including affinity-specific surfaces. Most soft-landing work has involved instruments specially constructed for these experiments. Extension to analytical mass spectrometers in widespread use may appear unlikely. However, it is these analytical mass spectrometers coupled with ionization sources such as liquid secondary ion mass spectrometry (LSIMS) and electrospray ionization (ESI) that have been used in formation of novel cluster ion species [16] high mass peptide ions, and unique ions that represent noncovalent interactions between reactive partners, such as enzymes and their substrates. It is these ions and these instruments that would seem to hold the most promise for soft-landing experiments of new and different types.

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Dedicated to the memory of B.S. Freiser, who taught me that it's a small planet but a fun one.

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One possible approach to new soft-landing experiments with novel ions may be to adapt ionization sources, such as LSIMS or ESI, to specialized soft-landing instruments. A second approach, adopted here, is to modify commercial analytical mass spectrometers to perform the soft-landing experiment. Such modifications should not alter the fundamental performance of the mass spectrometer, nor should they prevent its routine use for mass spectral analysis. This second approach is unlikely to achieve the high ion fluxes that can be processed through a specialized soft-landing instrument, but this limitation may be offset by the novelty of the surface prepared, and the widespread distribution of such instruments. In this article, we describe the modification of a hybrid geometry tandem mass spectrometry instrument for soft-landing experiments, and present first results that document the success of this soft-landing experiment.

2. Experimental

Hybrid geometry tandem mass spectrometry instruments (EBqQ) [17] were developed specifically for tandem mass spectrometry experiments to combine the performance of a double focusing, sector-based instrument with the capabilities of a multiple quadrupole instrument for tandem mass spectrometry. In the case of our VG-SEQ instrument, electric and magnetic sectors (EB) are followed by an rf-only quadrupole collision cell and a final mass-analyzing quadrupole. This hybrid instrument is fitted with two detectors. The final detector (used for tandem mass spectrometry experiments) is located at the end of the beam line after the mass-analyzing quadrupole. For use as a double focusing mass spectrometer, the intermediate detector is used. This intermediate detector is positioned after the magnetic sector, but before ion deceleration into the rf-only quadrupole collision cell. In the VG 70-SEQ mass spectrometer, this intermediate detector operates on the principle of diversion of the ion beam from its straight-line path by imposition of a voltage on a deflection dynode. The deflected ion beam then hits a scintillator, and the emitted light is detected. The axis of the deflection dynode and scintillator detector is orthogonal to the path of the ion beam. The deflection dynode is itself mounted to a support attached to a standard 2.75 in. vacuum flange. The location of this flange was ideal for placement of a collection surface to intercept the mass-analyzed beam that exits from the sector portion of the mass spectrometer (Fig. 1).

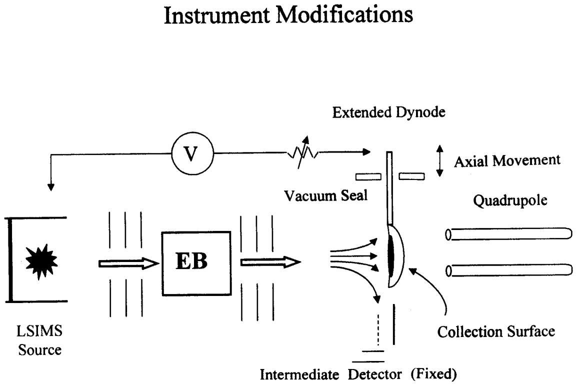

Fig. 1. Instrument modifications to a VG70-SEQ for the soft-landing experiment.

The modifications to transform the VG 70-SEQ mass spectrometer into a soft-landing instrument should maintain the ability to use a low deflection potential to deflect ions into the intermediate detector and also provide an axial movement so that a collector surface can be moved to intercept the beam. The potential on the collection surface must be able to vary from a few volts below the source accelerating potential to that of the accelerating voltage itself (8000 V on the VG hybrid instrument). Finally, a means to remove the modified surface from the instrument must be provided.

The design of the collection probe is a modification of a direct insertion probe fitted to the 2.75 in. vacuum flange. Axial and radial motion is accomplished via the standard sliding seal that also provides electrical insulation so that the deceleration potential can be placed on the collection surface. Probe designs include electrical leads for a connection to the sample heater; such was the case here, and these leads can be used to carry the deceleration potential. The potential applied to the stainless steel collector surface is slaved to the source accelerating voltage itself to ensure proper tracking. Modest machining of the probe tip was necessary to secure the collection surface to it. A threaded bolt connection sufficed to make the single connection to the slaved source potential, or the usual deflection voltage. The sliding vacuum seal displayed sufficient insulation so that no arcs were observed. The pressure in the region of the intermediate detector is approximately 5×10^{-7} Torr.

One of the primary concerns to be addressed in the use of an analytical beam instrument for soft-landing experiments is the ion flux through the instrument from the source through to the collection surface. A sector instrument is designed to maintain a high ion transmission from the source to the detector. In the soft-landing experiment, the magnet is set to pass only the mass-to-charge ratio of the ion of interest or a small window of ion mass, through to the collection surface. The slits along the ion path allow the appropriate tradeoff between mass resolution (dispersion) and sensitivity (transmission) for this ion beam. Therefore, one of the first tasks in our program of instrument modification was to establish ion transmission through the instrument at various slit settings. These measurements were entered into a spreadsheet program that predicts ion flux at the position of the collector surface for any given combination of slit settings [18]. A separate article describes the basics of this program, and includes the details of a full spreadsheet calculation [19]. Prior to any instrument modification, detected ion currents at a number of different slit settings were recorded, using a count and flux of ions from the source. Sector transmission could not be independently measured. Instead, a reasonable value was assumed in the initial spreadsheet calculations, and then quantitative analysis of the collected ions was used to correct the overall predicted ion transmission value. The ion flux (in ng) can be determined by multiplying the mass of the ion (Daltons) by the intensity of the ion beam (ions/seconds summed across the selected mass window) with appropriate conversion factors. Ion beams of interest may differ greatly in intensity. Some of the novel ions from the source may be those formed in ion/molecule or clustering reactions, and may be of lower relative intensity in the mass spectrum. For example, using the measured intensity of one of the larger ions in the LSIMS mass spectrum of a metal acetylacetonate solution, the spreadsheet predicts an ion flux of 1.08×10^{-2} ng/s onto the collection surface with a source ion intensity of 7.80×10^{7} counts/scan. This calculation was based on the slits being completely open, corresponding to a mass resolution at baseline of 1000. After first experiments were successfully completed, several quantitative ion collection runs were made to provide a calibration factor.

Ideally, the source flux for ions of interest should be constant. A constant but low ion flux can be achieved in electron ionization, chemical ionization, and ESI, but ion intensities in LSIMS can vary substantially with the time of bombardment [20,21]. For many ions, an initial high intensity is followed by an exponential decay. Switching primary ion beam bombardment on and off may regenerate an intense sample ion beam, but eventually the sample solution will be depleted. A continuous flow sample introduction [22], with repetitive introduction of aliquots of the sample solution, provides a convenient means to maintain a high flux of sample ions from the source. Such a sample introduction system also provides a convenient means to introduce different ions in sequence onto a surface, with the ultimate promise of generating a layered surface of defined morphology. In the work described here, positive ion LSIMS spectra and ESI mass spectra are obtained using standard source, solvent, and matrix parameters.

3. Results and discussion

First experiments must document that ions can indeed be transferred from the source, through the mass spectrometer, to the collection surface. This led to a consideration of means that could be used to characterize surface species, given that initial experiments were likely to collect only a small absolute amount of sample. Our recent work had documented creation in an LSIMS experiment of multimetal and mixed metal cluster ions containing Ga, In, and V from solutions of metal acetylacetonates in triethanol-

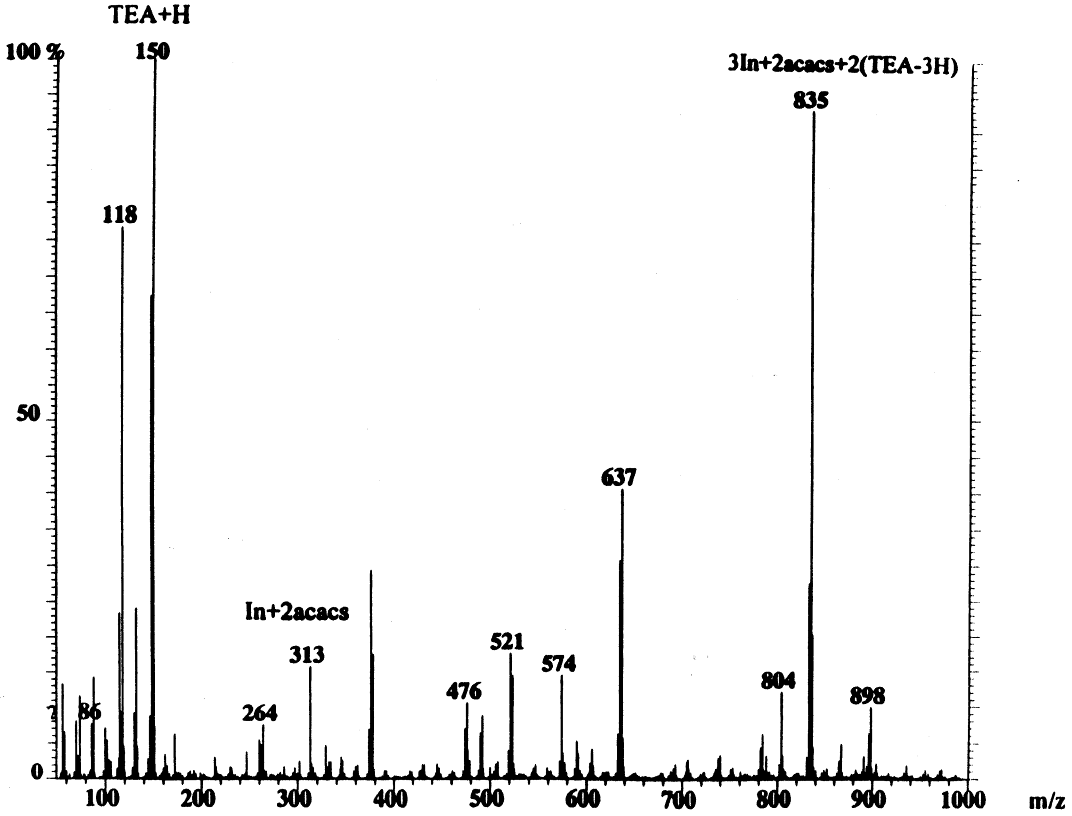

Fig. 2. Positive ion LSIMS mass spectrum of In(acac)$_3$ in the presence of triethanolamine.

amine (TEA). The high sensitivity of inductively coupled plasma/mass spectrometry (ICP/MS) allowed us the best chance for documenting initial success, even though the structure of the ion would not be revealed. Additionally, the actual energy at which a soft-landing could be achieved for such a novel cluster ion could not be predicted. Use of the non-structural specific analyses allowed the quantitative aspects of the transfer to be documented. A solution of In(acac)$_3$ was prepared in dimethylsulfoxide and acetonitrile solvents, and the solution was mixed with TEA and sputtered by a cesium ion beam. We chose the ion at m/z 835, representing $[3\ \mathrm{In} + 2\ (\mathrm{TEA}\text{-}3\mathrm{H}) + 2(\mathrm{acac})]^+$, from the positive ion LSIMS mass spectrum (Fig. 2) of this solution. The magnetic sector was set to scan a range of 20 Daltons width around the ion at m/z 835. The choice of a 20 Da window rather than a single mass was prompted by two factors. The first is the desire to include all isotopes of the metals, assuring the maximum efficiency for cluster ion formation. The second is our initial uncertainty as to how stable the mass calibration would be over an expected run time of hours, and linkage of the source voltage to the collection surface. The use of higher mass resolution in the selection of the preparative ion beam means that only a specified isotopic composition for the ion is passed to the surface, itself the basis for intriguing future experiments. The potential difference between the collector surface and the source accelerating voltage was approximately 1 V in these initial experiments. With the slit settings used, the spreadsheet predicted that an ion flux (source intensity of 7.8×10^7 counts/scan) collected for 240 min. would correspond to a total of 156 ng of the metal cluster collected on the surface, assuming 100% efficiency.

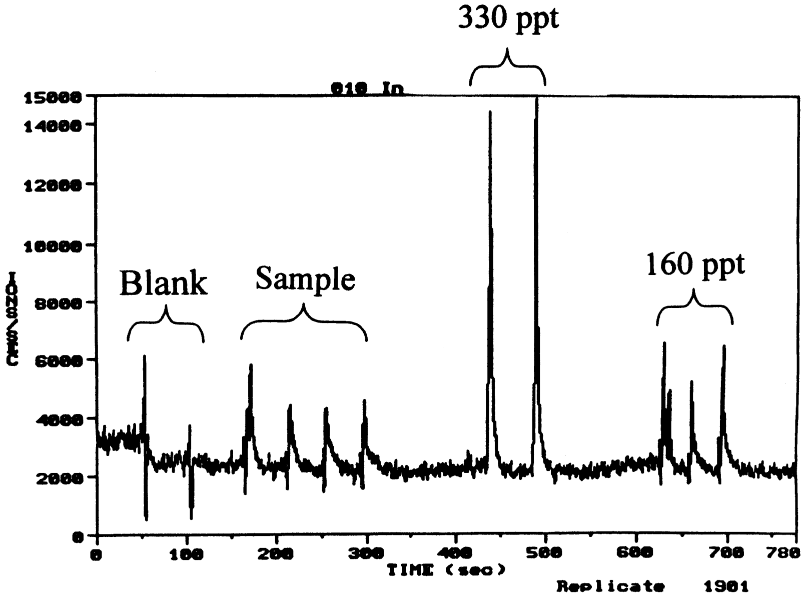

Fig. 3. ICP-MS of the methanolic wash with 5% HCl of the collection surface. The time axis represents intervals between analysis of replicate or sequential samples.

Using ICP/MS as the detection method, the presence of the indium on the collection surface was confirmed. Fig. 3 shows the result of the ICP/MS analysis of the methanolic wash (5% HCl) of the collection surface. Standards of indium at concentrations of 330 and 160 ppt were injected in succession at 45-second intervals. The time axis represents successive replicate analyses and changes in sample

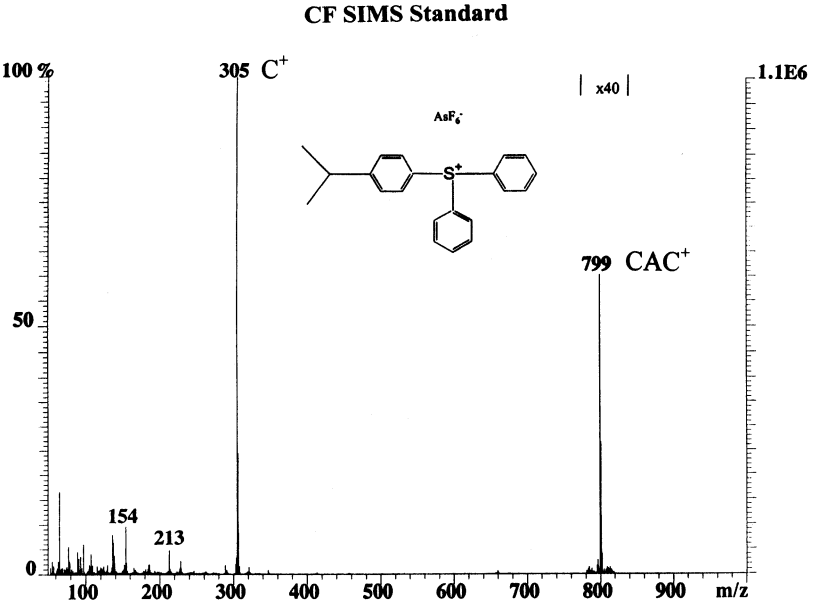

Fig. 4. CF-SIMS mass spectrum of sulfonium salt S in MeOH and 1% NBA.

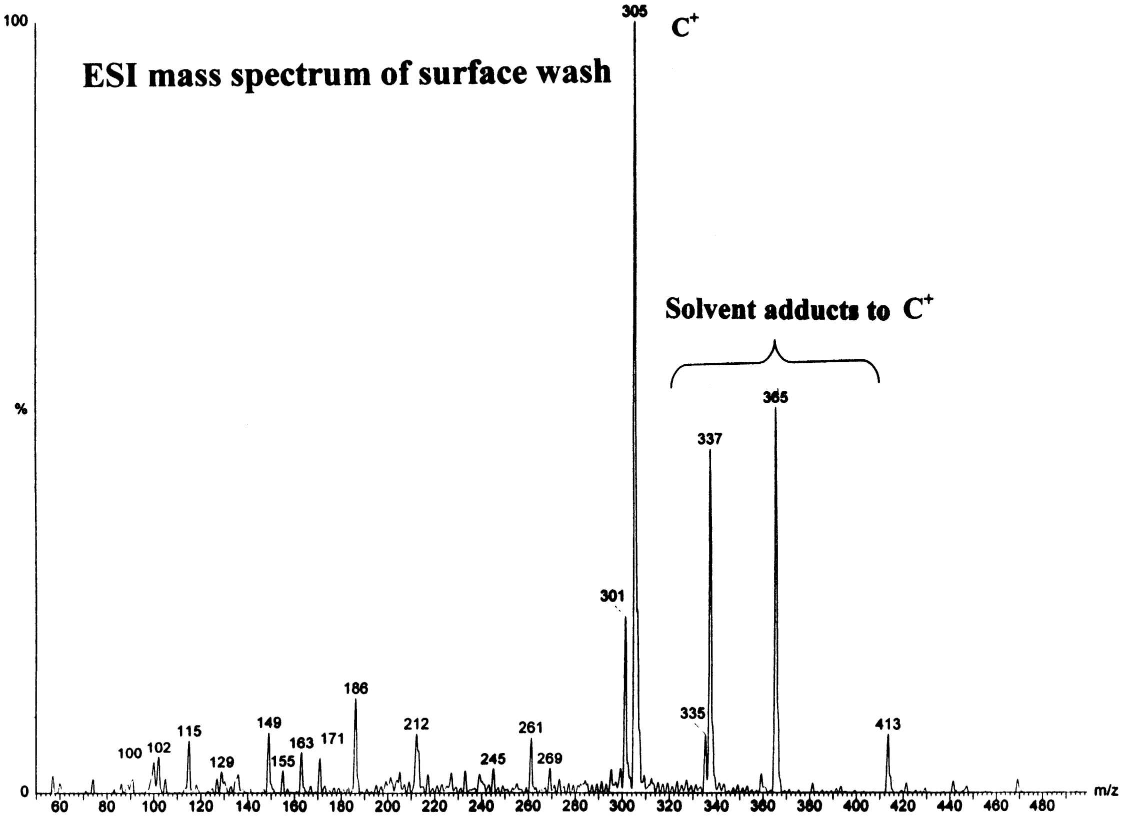

Fig. 5. Positive ion ESI mass spectrum of methanolic wash of the collection surface.

solution. The presence of indium on the surface is confirmed. We do not know the ion structure, but since the magnetic sector was scanned from *m*/*z* 825–845, we are assured that the In atoms reached the surface as part of the [3 In + 2 (TEA-3H) + 2(acac)]$^+$ ion. The blank is a surface wash that shows there was no In background on the collection surface.

Deceleration of the ions before collection on the surface should preserve the structure of the ion; this is the essence of the soft-landing experiment. We used continuous flow SIMS to create intense cations from an organic sulfonium salt, whose structure is given in Fig. 4; the peak at *m*/*z* 305 corresponds to the intense cation (C^+). We used a continuous flow sample introduction to maximize the ion flux of the ion at *m*/*z* 305 from the source. Otherwise, the LSIMS spectrum fades after 2–3 min. as the support matrix evaporates. The stage is set for success in that sulfonium salt cations do not exhibit much fragmentation in LSIMS. They are robust ion candidates for a soft-landing experiment. For this experiment, the potential difference between the collector probe and the source accelerating voltage was again less than 1 V to assure soft-landing of the ion. The magnet was set to scan a 10 Da window (*m*/*z* 300–310) of ions. The mass range was tightened, however, the reasons for scanning a mass-to-charge ratio range are as before. Positive ion ESI/MS was used to analyze the methanolic wash of the collection surface after the soft-landing experiment. The ESI mass spectrum and the MS/MS spectrum of the methanolic wash matched those of the standard sample, confirming that the structure of the cation was preserved in the soft-landing experiment (Fig. 5). The ion at *m*/*z* 305 has an intensity of 1.1×10^8, which corresponds to a collection of 168 ng (12 h of deposition), of the intact

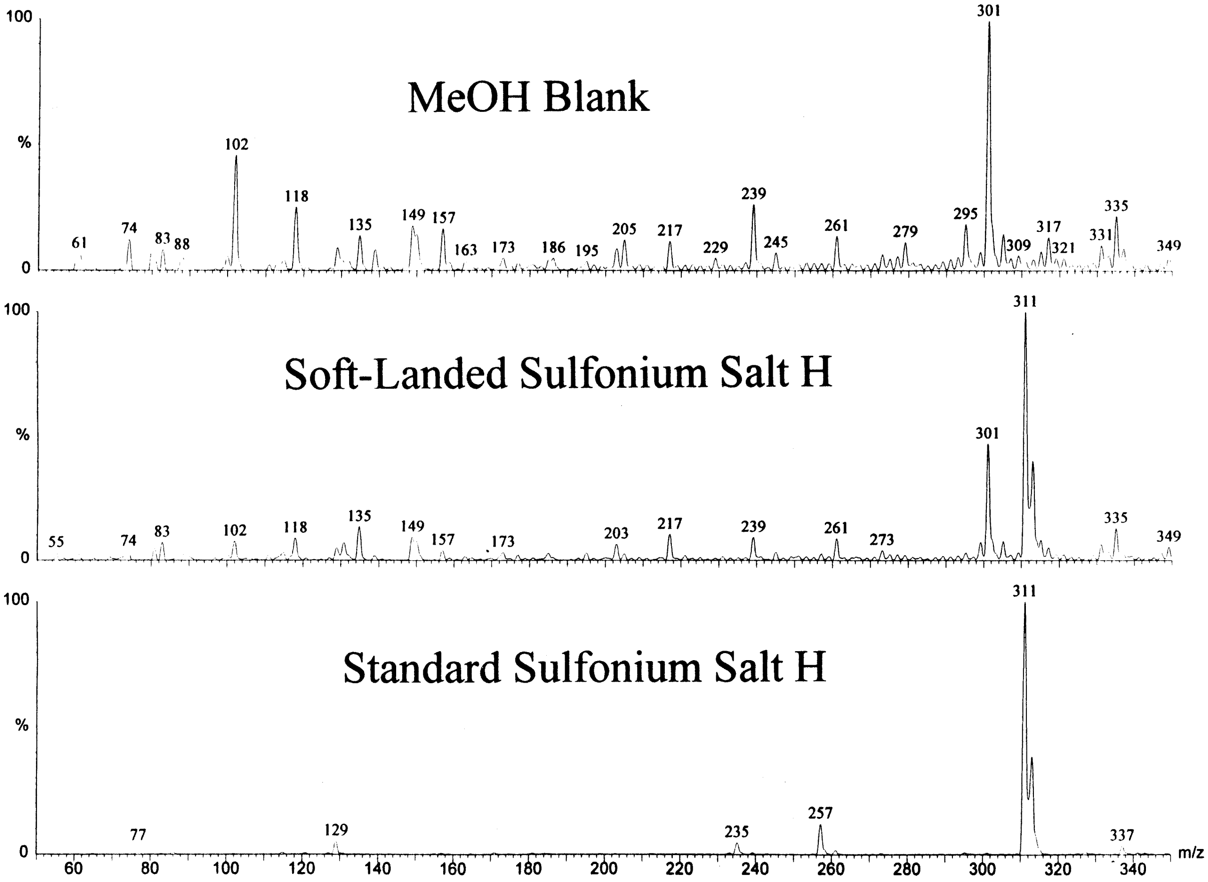

Fig. 6. Positive ion ESI mass spectra of sulfonium salt H.

cation on the surface. A second organic sulfonium salt was successfully deposited on the surface in a test of experiment reproducibility. The positive ion ESI mass spectrum and the MS/MS spectrum of the methanolic wash matched those of the original sample, confirming that the cation was preserved in the soft-landing experiment (Fig. 6). The intensity of the ion at *m*/*z* 311 is 6.4×10^7, which corresponds to a collection of 162 ng of the intact cation on the surface. These experiments suggest that our transmission spreadsheet is reproducible to about ±20%.

4. Conclusions

The sulfonium salt experiment described above shows that the structure of an organic species deposited on a surface can be preserved if the kinetic energy of impact is sufficiently low. At higher incident kinetic energies, the process of surface-induced dissociation occurs, as has been thoroughly studied [23]. In analogy to the static SIMS experiment [24], the flux of ions to the surface should be kept low so that an ion once deposited will not be disturbed by a second incoming ion. Such overlaps could disrupt homogenous coverage, as well as possibly induce structural dissociation. We calculate the static SIMS limit for the collection surface to correspond to a flux of 8.7×10^{-3} ng/s onto the surface for the indium acac adduct ion, with an assumed ion size of 50 Å, suggested by molecular modeling experiments [16]. Our collection rate for this ion at *m*/*z* 835 is 6.1×10^{-6} ng/s, well below the static SIMS limit.

Analysis of blanks, that is metal surfaces placed within the intermediate detector region but not used as collection targets, reveals that these surfaces are not clean but covered with a hydrocarbon film. We surmise that this film is attributed to the background of pump oil contamination throughout the instrument. At a pressure of 5×10^{-7} Torr, the surface is of course instantly coated with such a background. We speculate that the presence of such coverage may aid in the soft landing of ions by providing an additional cushion as the ion approaches. The strong intermolecular forces that might be expected between an ionic projectile and an atomically clean surface may be damped by this relatively nonpolar and easily displaced molecular layer. It has been suggested that the "dirtiness" of the system is in fact the key to the success of these experiments. If so, the phrase "matrix-assisted deposition for nano-engineered surface structures" may be appropriate for our experiment.

We have considered the effect of the shape of the collection surface on the collected ion density. A collection surface angled or curved with respect to the incident ion beam will exhibit a range of expected coverage densities for collected species, as will a curved collection surface. A ramped deceleration voltage, used in conjunction with a flat collection surface, is predicted (via the SIMION ion optics program) to create a graded circular collection pattern. With careful control of the deceleration potential, a central core of the more energetic impacts (higher degree of incident ion fragmentation) can be surrounded by a buffer zone of soft-landed sample ions that can retain the original ion structure. Implications for engineered surfaces, with isolated reactive areas on the scale of a few nm in diameter, should be evident.

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