Peer-Reviewed Abstract

Use of High Energy Collision Induced Dissociation (HE-CID) in TOF-SIMS for Unambiguous Peak Identification and Imaging

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1. Introduction

A new tandem TOF-TOF imaging mass spectrometer exploiting the unique characteristics of the TRIFT analyzer used in the PHI *nanoTOF* II has been developed [1,2]. This design allows for conventional TOF-SIMS spectra and MS/MS spectra of a specific precursor to be acquired in parallel, providing the maximum information from a given analytical volume. It has been recognized for many years that MS/MS was required in TOF-SIMS to unambiguously identify peaks above *m/z* 200 due to the limitations of mass accuracy. Previous tandem mass spectrometry designs used for TOF-SIMS [3,4] and MALDI [5] have discarded all secondary ions except the precursor when performing an MS/MS experiment. In the design reported here, a single nominal mass can be selected from the stream of secondary ions after it emerges from the 3rd ESA and deflected into a collision cell for high energy collision induced dissociation (HE-CID).

2. Results and Discussion

Figure 1 illustrates how a single mass is selected from the stream of masses in the standard TOF-SIMS spectrum and deflected into a collision induced dissociation (CID) cell where the molecular ion is fragmented by high energy (1.5 keV) collision with argon gas. After fragmentation in the CID cell, the ions are further accelerated into a linear TOF analyzer and recorded at the MS2 detector.

This new capability for peak identification can be used for any application of TOF-SIMS where unambiguous identification of high mass ions is required. One example is for identification of surface contamination and additives on the surface of polymers. A TOF-SIMS spectrum from the surface of a commercial polypropylene (PP) sheet is shown in Figure 2 (top). The mass accuracy of TOF-SIMS is not sufficient to unambiguously identify the peaks above *m/z* 200 by their measured exact mass. The low mass region show peaks not representative of PP such as Na^+, K^+, $C_3H_8^+$, $C_7H_7^+$, and $C_9H_{12}N^+$. However, it is not clear which high mass molecular ions these fragments came from. The MS/MS spectrum of the peak at *m/z* 304 is shown in Figure 2 (bottom). It shows that the molecular ion at *m/z* 304 fragments to produce *m/z* 58 ($C_3H_8N^+$), m/z 91 ($C_7H_7^+$), and *m/z* 212.

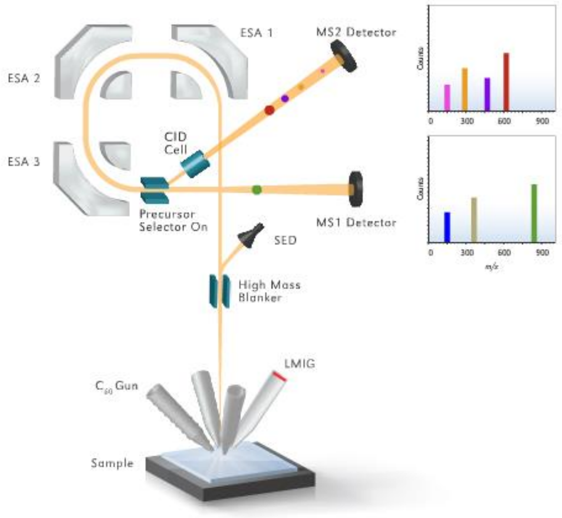

Fig. 1. (color online) A schematic of the PHI *nanoTOF* II equipped with MS/MS.

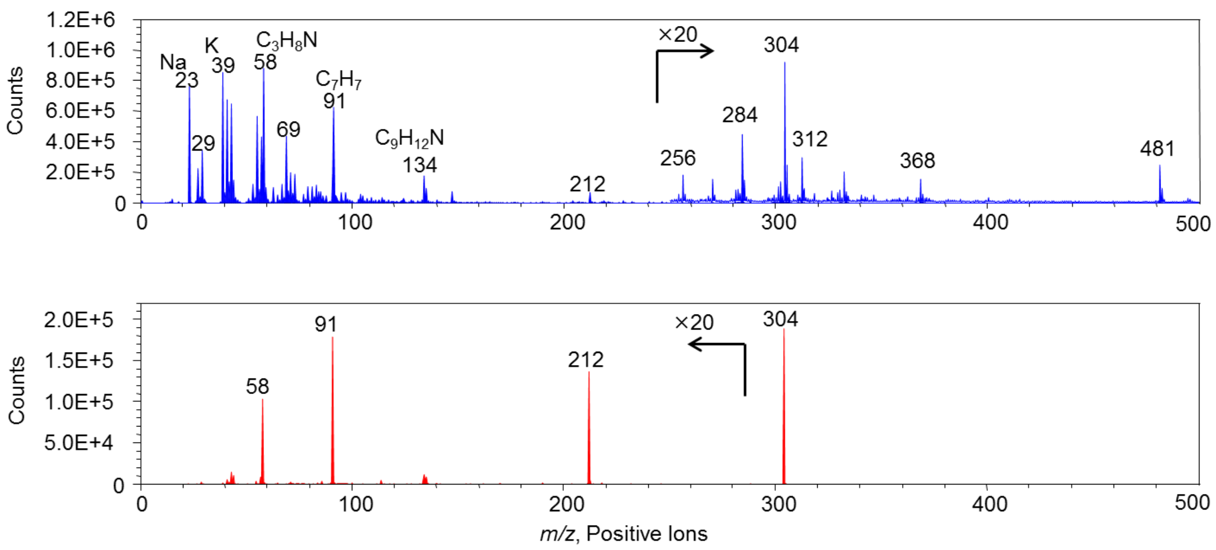

Fig. 2. (color online) (top) A TOF-SIMS spectrum from the surface of a polypropylene film containing impurities or additives above *m/z* 200; (bottom) MS/MS spectrum of *m/z* 304.

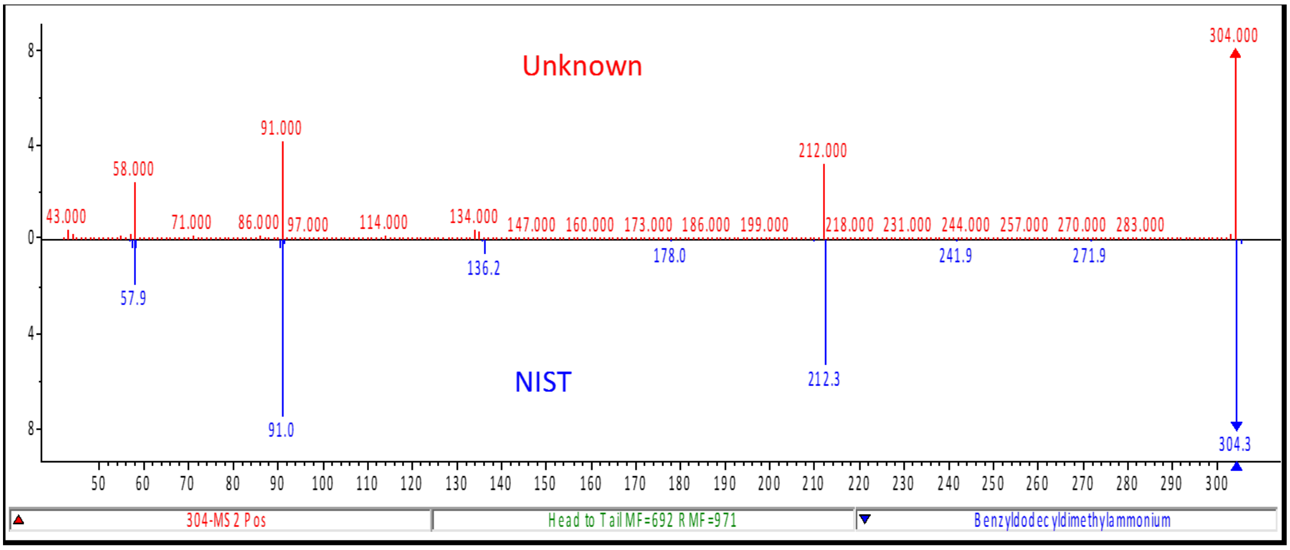

Fig. 3. (color online) Comparison of the MS/MS spectrum of *m/z* 304 from the PP surface (top) with the reference spectrum of Benzyldodecyldimethylammonium in the NIST v14 database.

Once a MS/MS spectrum is obtained it can be imported into the NIST v14 MS/MS library for identification. Figure 3 shows the match between the acquired MS/MS spectrum of *m/z* 304 from the surface of PP (top) and the reference spectrum of the closest match in the NIST database (bottom). The major fragments at *m/z* 58, 91, and 212 all match allowing the identification as benzalkonium, a cationic surfactant.

Once the identification is known using database matching or by proposing a structure, it is easy to verify the fragment ions make sense by simple bond cleavages of the proposed structure as shown in Figure 4. Because the fragmentation pattern in MS/MS is from a single mass that has been isolated from all the other molecules detected in the TOF-SIMS spectrum, spectral database matching becomes much easier and more accurate.

The linear TOF used for MS/MS can be acquired at high speed, making it practical to perform MS/MS

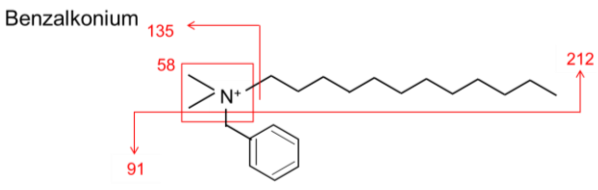

Fig. 4. (color Online) Assignment of peaks in the *m/z* 304 MS/MS spectrum based on simple bond cleavages.

analysis in the imaging mode without slowing down the repetition rate of the primary ion beam. Just as with standard TOF-SIMS data, a MS/MS spectrum is saved for every pixel in the image. This allows images to be constructed from any fragment ion in the MS/MS spectrum. In addition, MS/MS spectra can be generated from any region-of-interest in the image.

3. Conclusion

Adding MS/MS capability to TOF-SIMS has made it possible to unambiguously identify molecular ions above *m/z* 200 for the first time. The ability to select a single mass in the TOF-SIMS spectrum for MS/MS analysis greatly simplifies data interpretation and will be especially useful for samples with complex surface compositions.

4. References

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