Advanced Spectra Interpretation in TOF-SIMS "Parallel Imaging MS/MS"

Shin-ichi IIDA[*1], Gregory L. FISHER[*2] and Takuya MIYAYAMA[*1]

[*1] ULVAC-PHI Inc., 370 Enzo, Chigasaki, Kanagawa, 253-8522, Japan
[*2] Physical Electronics Inc., 18725 Lake Drive East, Chanhassen, MN 55317, USA

Recently, the applications of TOF-SIMS have expanded into a wide variety of organic materials, because the sensitivity of high mass molecular ions was improved dramatically. However, it was very difficult to determine the chemical formula from the measured mass above m/z 200. The ambiguous peak identification was a significant problem in TOF-SIMS. In order to determine the chemical formula as well as detailed chemical structure, we developed the TOF-SIMS instrument equipped with Tandem MS (MS/MS), and applied it to analysis of various organic materials. In this article, we will introduce this unique instrument, and demonstrate the results of the spectra analysis using MS/MS.

1. Introduction

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is a technique that provides the information of molecular species on the outermost solid surface with high sensitivity and high spatial resolution. This technique has been widely used for analyzing the chemical structures of various organic materials, such as rubber, plastics, fibers, medicines and biological samples. Since the increased sensitivity of high mass ions by Bi, Au LMIG (Liquid Metal Ion Gun) and commercialization of fullerene and Ar gas cluster ion beam (Ar-GCIB) which can sputter without significant molecular damage[1-3], the organic depth profiling as well as three dimensional analysis using TOF-SIMS have been rapidly expanding[4-6]. Nowadays, TOF-SIMS is considered to be a powerful analytical technique for organic materials analysis. However, this rapid expansion of organic applications has resulted in a serious problem regarding the spectrum interpretation. When it comes to identify an unknown molecular ion peak with the mass above m/z 200 by using current conventional TOF-SIMS instrument, it is quite difficult to determine the chemical formula. Spectrum interpretation is necessary to identify the chemical compounds on a surface, the difficulties of peak identification have been a big challenge on TOF-SIMS analysis[7]. To solve this problem, we have developed TOF-SIMS instrument equipped with tandem mass spectrometer (MS/MS)[8], and attempted to identify the chemical structures of unknown organic materials[9, 10]. This article describes the newly designed MS/MS system and its features, and results of compound identifications of unknown organic materials to determine the chemical formula.

2. TOF-SIMS instrument equipped with "Parallel Imaging MS/MS"

2.1 Challenge on TOF-SIMS spectrum analysis

Figure 1 shows an enlarged negative ion spectrum around m/z 282 from a contaminated film. The peak was detected around m/z 282, while it was not detected in a
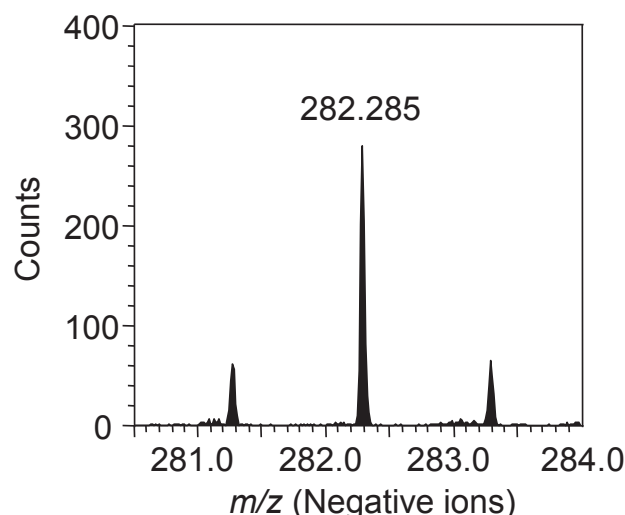

Figure 1　TOF-SIMS spectrum of contaminated surface. The mass region around m/z 282 was expanded.

Table 1　The list of possible chemical formula when we assume that the peak consists of H, C, N, and O.

Formula	Mass [m/z]	Deviation [$\times 10^{-3}\ m/z$]
$C_{18}H_{36}NO$	282.27949	5.51
$C_{17}H_{36}N_3$	282.29073	-5.73
$C_{16}H_{34}N_4$	282.27816	6.84
$C_{19}H_{38}O$	282.29206	-7.06
$C_{17}H_{34}N_2O$	282.26692	18.08
$C_{18}H_{38}N_2$	282.30330	-18.30
$C_{15}H_{32}N_5$	282.26559	19.41
$C_6H_{28}N_{13}$	282.25887	26.13
$C_{18}H_{34}O_2$	282.25568	29.32
……	……	……

clean film spectrum. The accurate mass of the peak was 282.285. Table 1 lists the chemical formula in the order of deviation from measured mass (=282.285) when we assume the peak is composed of ^{1}H, ^{12}C, ^{14}N, and ^{16}O. However, we cannot determine the right one from them, moreover, we don't know whether we should take other elements into consideration or not. This difficulty in peak identification is the biggest challenge of TOF-SIMS analysis, and a breakthrough idea is needed to overcome this situation.

2.2 Parallel Imaging MS/MS

The schematic diagram of conventional TOF-SIMS instrument (PHI nanoTOF II) is shown in Figure 2(a). When the pulsed ion beam irradiates onto the sample sur-face, secondary ions are emitted from the surface. The secondary ions are introduced to the mass analyzer by the extraction electrode, then fly and reach detector. The arrival time of secondary ions depend on its mass weight. By utilizing the time difference of among secondary ions, it is possible to carry out the mass separation, and then generate the mass spectrum. The secondary ions emitted from the sample surface have distributions of initial energy and angle, therefore, time differences will be generated even if they are the same mass. The three electrostatic analyzers (ES1, ES2 and ES3) can compensate the time differences[11]. The interval between primary ion pulses is determined by the mass range. In TOF-SIMS measurements, the mass range from 0 to 2000 Da is generally used. In this case, the pulse interval is ～125 μs (the
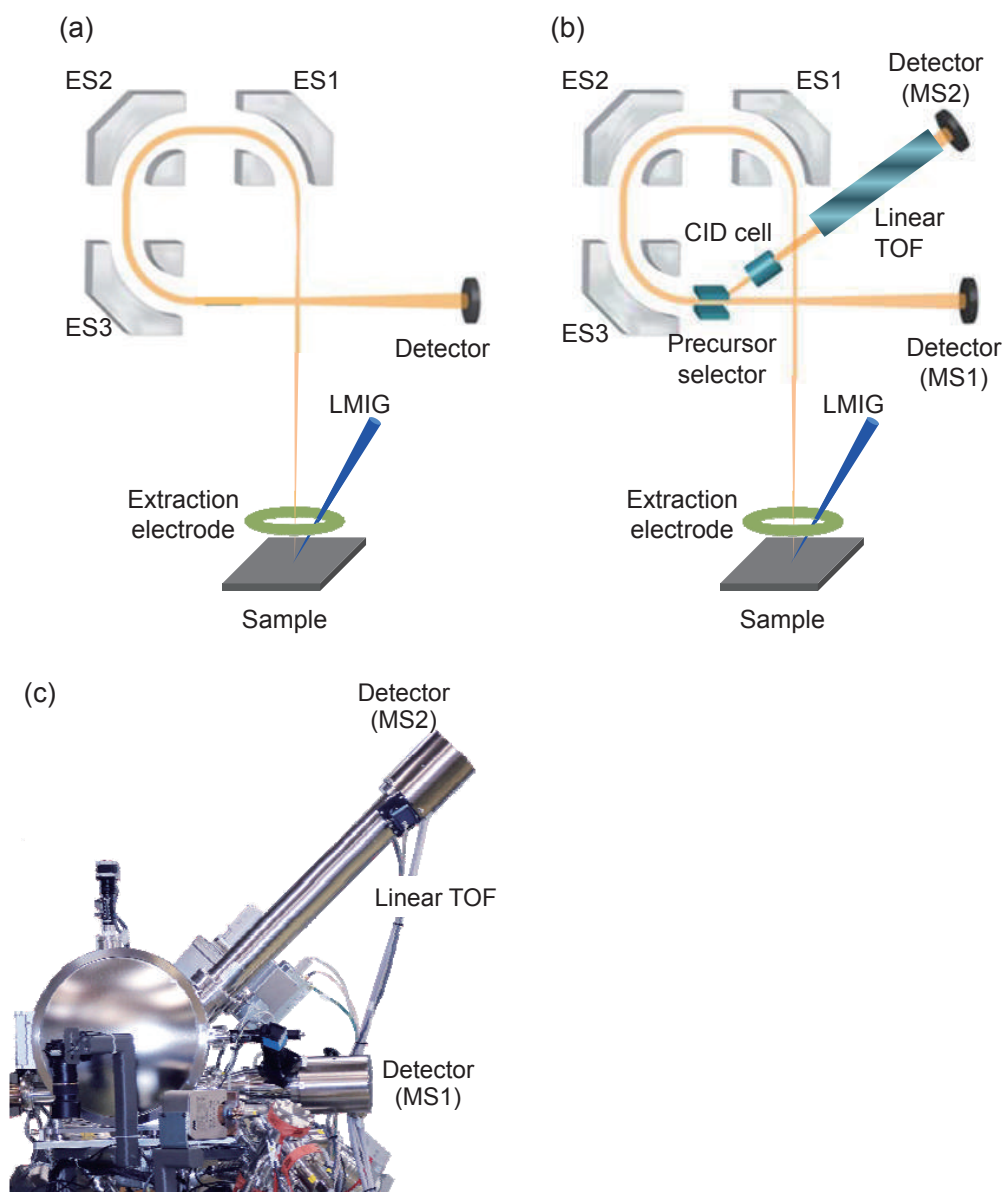

Figure 2   Illustrations of (a) conventional TOF-SIMS instrument, and (b) newly designed TOF-SIMS instrument with parallel imaging MS/MS. (c) Overview of parallel imaging MS/MS.

pulse frequency is ～8000 Hz). In commercial TOF-SIMS instrument, the mass resolution ($M/\Delta M$) is ～10,000 and liquid metal ion source, which can easily achieve the small probe size less than 100 nm, is commonly used. By scanning the fine tuned ion beam on the sample and recording the spectrum information at each point, TOF-SIMS can give us high resolution image. This is the summary of conventional TOF-SIMS instrument.

On the other hand, the schematic diagram of a TOF-SIMS instrument equipped with the Parallel Imaging MS/MS and its photo are shown in Figure 2 (b) and (c). The precursor selector, collision-induced dissociation (CID) cell and linear TOF are integrated to conventional mass analyzer. The specified secondary ions within 1 Da mass range can be selected by the precursor selector. The selected secondary ions are introduced to the CID cell with an energy of 1.5 keV. The inside of CID cell is filled with high pressure Ar gas, the molecular ions are dissociated during passing through the CID cell. After the dissociation, the mass weight of the fragment ions is measured by the linear TOF. This system has two mass spectrometers (MS1 and MS2), and two different types of spectra are obtained. To distinguish two spectra, we defined MS^1 spectrum and MS^2 spectrum respectively. Thanks to the parallel acquisition design, this instrument can provide both MS^1 and MS^2 spectra simultaneously, while general MS/MS instruments cannot. In addition, it can take data as fast as conventional TOF-SIMS instruments, because the pulse frequency is the same (～8000 Hz) as conventional instrument, even in the MS^2 spectrum acquisition.

3. Applications of Parallel Imaging MS/MS

3.1 Samples

In this study, we used three kinds of samples: (1) commercially available polyethylene terephthalate (PET) film (Teijin Dupont Film Ltd.), (2) unknown organic material with several organic components mixture, and (3) industrial plastic which includes many unknown additives.

3.2 Measurement conditions

We used 30 keV Bi_3^+ ions for TOF-SIMS measurement. The total acquisition time was (1) 2 minutes, (2) 14 minutes, and (3) 8 minutes. 15 eV electrons were used for charge neutralization on the sample surface. The TOF-SIMS measurement was completed within a static limit (5 $\times 10^{12}$ ions/cm^2 or lower), and it was confirmed that the secondary ion intensity was constant during the measurement.

3.3 Comparisons between MS^1 and MS^2 spectra

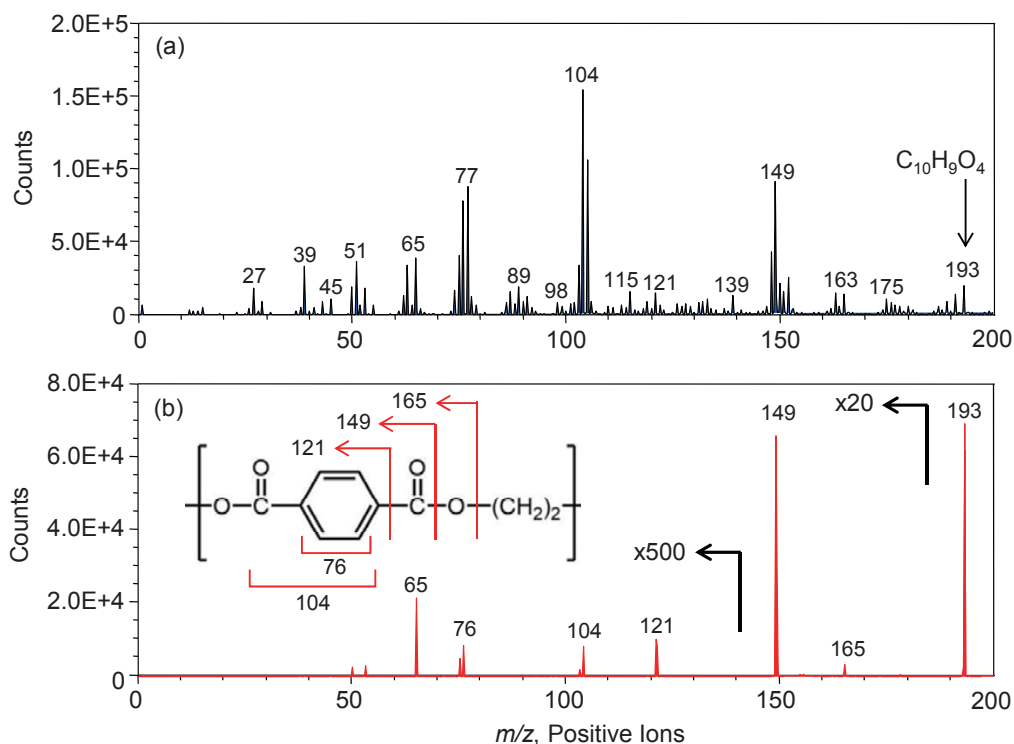First of all, we compared MS^1 and MS^2 spectra of PET

Figure 3　(a) MS^1 spectrum obtained from a clean PET (polyethylene terephthalate) surface. (b) MS^2 product ion spectrum obtained from protonated PET monomer ion (m/z 193).

film to clarify the differences. Figure 3(a) shows the MS^1 spectrum of PET film surface after removing the surface contaminations by Ar-GCIB. Enormous number of fragment ions appeared in the spectrum although the pure PET film was used and then surface was cleaned. The presence of many fragment ions is one of factors that make it difficult to do the TOF-SIMS spectrum interpretation. The peak at m/z 193, as indicated by the arrow in the figure, was assigned to $C_{10}H_9O_4{}^+$, which is the protonated PET monomer ions. Figure 3(b) shows the MS^2 spectrum when we choose $C_{10}H_9O_4{}^+$ ions for MS/MS measurement. While the complicated fragment pattern was observed in MS^1 spectrum, MS^2 spectrum showed the very simple fragment pattern. This simple fragment pattern reflects the molecular structure (see Fig. 3(b)), and gives us the clue of peak identification directly. The MS/MS provides us the simple spectrum without any sample modification. Furthermore, we can extract any fragment peak from all components to MS/MS analysis. These are the advantages of MS/MS.

3.4 Organic material contained unknown components

Figure 4(a) shows the MS^1 spectrum of organic material contained several unknown components. As shown in the figure, it is possible to identify major peaks less than m/z 200. However, it is difficult to identify peaks with mass over m/z 200, even for known chemical composition. Among the peaks shown in this spectrum, we selected the peak of m/z 201 to analyze MS^2 spectrum. Figure 4(b) shows the MS^2 spectrum when we chose m/z 201 peak as a precursor ion. The spectrum indicates that the selected peak is composed of three molecules with masses of 77, 77 and 47 Da. It also indicates that these two molecules with 77 Da were not adjacent to each other because there was no peak at m/z 154 (= 77 + 77). On the contrary, the peak at m/z 124 (= 77 + 47) was detected in the MS^2 spectrum. These results suggested that two molecules of 77 and 47 Da were adjacent. From the exact mass of 77 and 47 Da, they were assigned to $C_6H_5{}^-$ and PO^- respectively. Thus, the peak observed at m/z 201 was found to be $(C_6H_5)_2PO^-$, and diphenylphosphine oxide (Figure 5). Both of the $C_6H_5{}^-$ and PO^- peaks were actually observed in the MS^1 spectrum, but the hints to solve the problem were hidden among the fragment ions of other components. That's the reason why it is quite difficult to predict
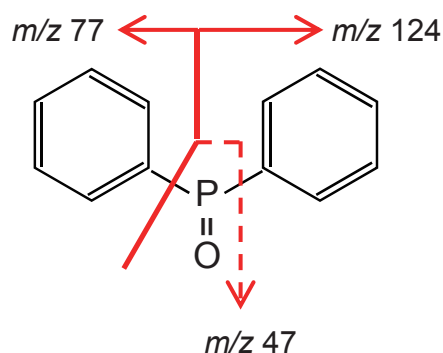

Figure 5 The result of chemical structure analysis of MS^2 spectrum shown in Figure 4. The unknown peak was found to be a diphenylphosphine oxide (DPPO).
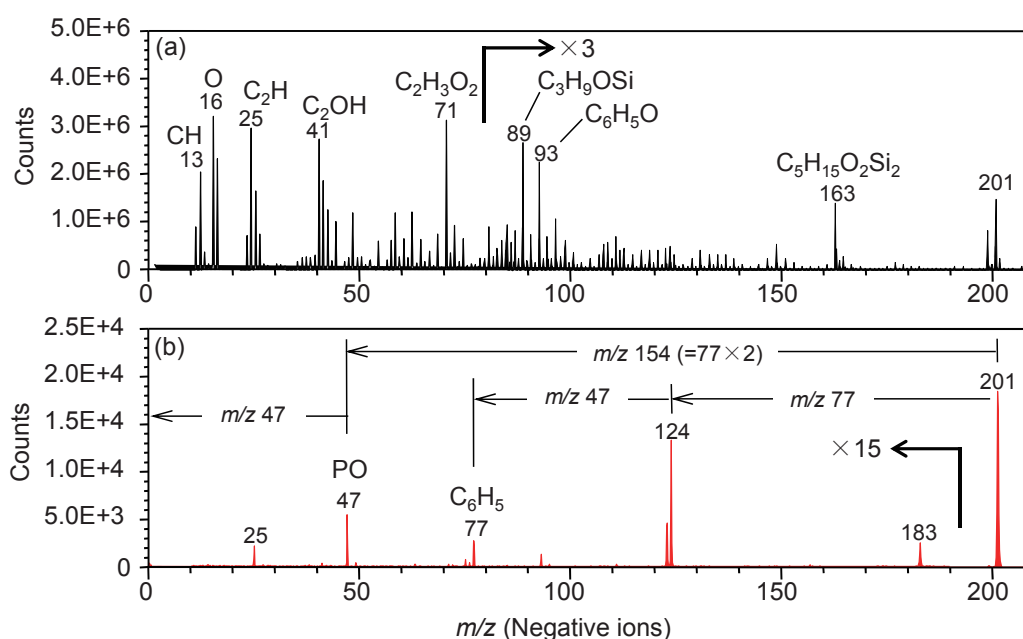

Figure 4 (a) MS^1 and (b) MS^2 spectra of unknown organic sample. MS^2 product ion spectrum was obtained by choosing m/z 201 as the precursor ion.

the chemical formula from MS^1 spectrum only. On the other hand, MS^2 spectrum can tell us the information of molecular structures directly. The circumstance of difficult peak identification in TOF-SIMS is much improved than before.

3.5　Industrial plastics

Generally, industrial plastics contain various kinds of additives, such as plasticizers, curing agents and fire retardants, etc. However, these additives segregate to the surface, and sometimes they give a bad effect to the product. For this reason, it is very important to understand what kinds of components exist on the plastic surface. Figure 6(a) shows a MS^1 spectrum of a plastic surface. As discussed above, it is difficult to identify peaks with mass over m/z 200, and it is impossible to distinguish each peak from base material, additive, or contaminant. Therefore, in this case, we attempted to take MS^2 spectra of m/z 284,

304, 332 and 481 which were significantly observed in the MS^1 spectrum. Figures 6(b) and 6(c) show the MS^2 spectra of m/z 304 and 481 respectively (The results of m/z 284 and 332 are omitted here). From the MS^2 spectral analysis using NIST tandem mass spectrum database[12], peaks at m/z 284, 304, 332 and 481 were assigned to Hexadecyltrimethylammonium, Benzalkonium, Benzyl Dimethyl Tetradecyl Ammonium and Tinuvin 770, respectively (Table 2).

Table 2　The results of compound identification from MS^2 spectrum analysis.

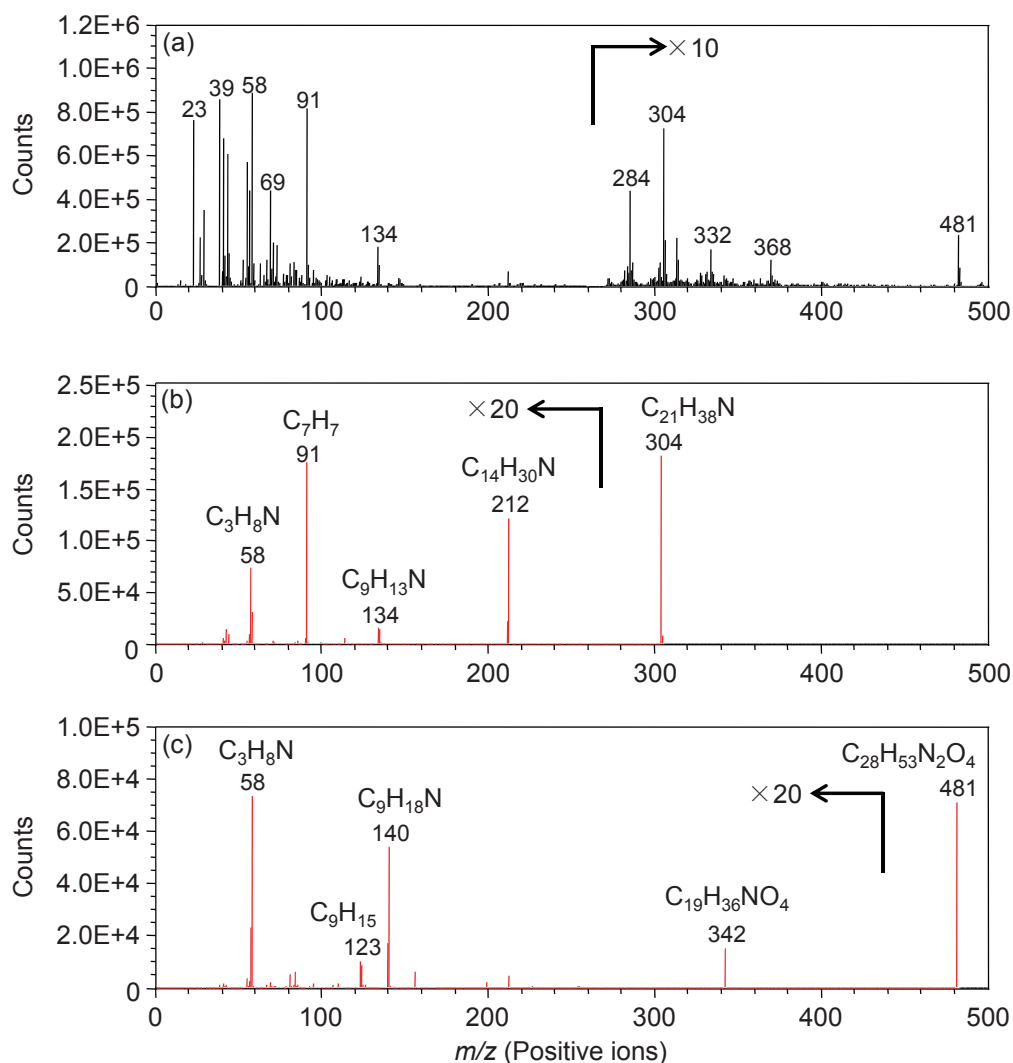| Mass [m/z]	Formula	Compound Name
284	$C_{19}H_{42}N$	Hexadecyltrimethylammonium
304	$C_{21}H_{38}N$	Benzalkonium
332	$C_{23}H_{42}N$	Benzyl Dimethyl Tetradecyl Ammonium
481	$C_{28}H_{53}N_2O_4$	Tinuvin 770

Figure 6　(a) MS^1 and (b), (c) MS^2 spectra of plastic surface. MS^2 product ion spectra were obtained by choosing (b) m/z 304 and (c) m/z 481 as the precursor ion, respectively.
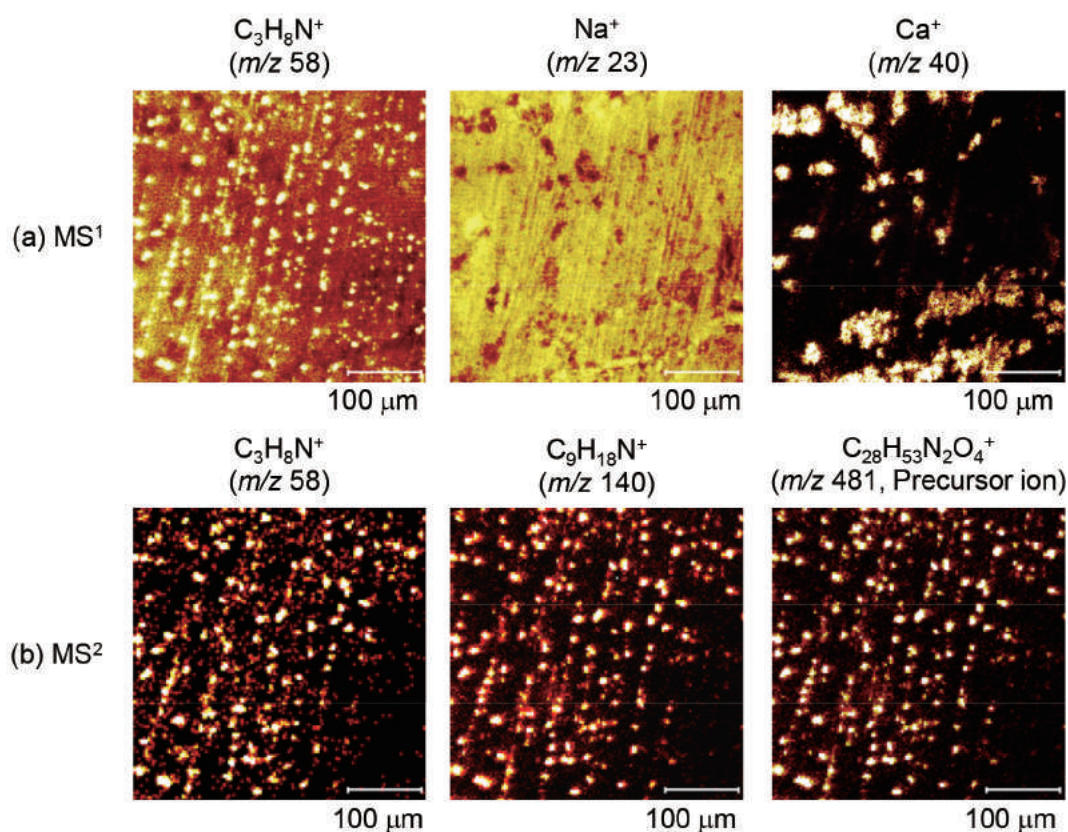
Figure 7　(a) MS^1 and (b) MS^2 images obtained from plastic surface.

Following the spectra analysis, MS^2 image analysis on the plastic surface was carried out. Figure 7(a) shows the MS^1 images of plastic surface, and Figure 7(b) shows the MS^2 images when we chose the peak at m/z 481 (Tinuvin 770) for MS^2 analysis. These MS^1 and MS^2 images were obtained from the same area at the same time. The field of view of the image was 400 μm × 400 μm. The MS^1 images reflect all the components while the MS^2 images show only extracted components. For example, $C_3H_8N^+$ (m/z 58) is detected in both of MS^1 and MS^2 images, but the distributions were different. This indicates that, in addition to Tinuvin 770, other molecules which have C_3H_8N structure exist on the surface. By comprehensive analysis among the MS^1 and MS^2 images, it is possible to do a detailed discussion on the distributions of each component on the surface.

This is an application example of Parallel Imaging MS/MS which provides both of MS^1 and MS^2 spectra and images simultaneously. It has demonstrated that the MS/MS makes it possible to identify molecular structures as well as to determine the chemical distributions on the surface.

5.　Conclusion

In this article, we firstly described the recent techniques and instrumentation of TOF-SIMS. Cluster ion beam technology enabled us to obtain the excellent applications of organic materials, however, the serious problem in peak identification has emerged. In order to solve the difficulty of spectrum interpretation, we have developed the Parallel Imaging MS/MS. The Parallel Imaging MS/MS provides the accurate chemical information on the outermost surface with high sensitivity in a short period. In the past, TOF-SIMS has been used as limited purpose because it could not reach the confident compound identification for unknown samples, but now TOF-SIMS equipped with MS/MS is expected as a promising tool to obtain the detailed chemical information, and it leads to the deep understanding about the surface chemistry.

References

1) N. Sanada, A. Yamamoto, R. Oiwa and Y. Ohashi: Surf. Interface Anal., 36 (2004) 280.
2) S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki and J. Matsuo: Rapid Commun. Mass Spectrom., 23 (2009) 1601.
3) T. Miyayama, N. Sanada, S. R. Bryan, J. S. Hammond

and M. Suzuki: Surf. Interface Anal., 42 (2010) 1453.

4) J. S. Fletcher, N. P. Lockyer, S. Vaidyanathan and J. C. Vickerman: Anal. Chem., 79 (2007) 2199.

5) G. L. Fisher, A. M. Belu, C. M. Mahoney, K. Wormuth and N. Sanada: Anal. Chem., 81 (2009) 9930.

6) S. Iida: KENBIKYO 48 (2013) 159.

7) S. Otomo, H. Itoh and Y. Abe: 18th International Conference on Secondary Ion Mass Spectrometry, (2011) p. 280.

8) P. E. Larsen, J. S. Hammond, R. M. A. Heeren and G. L. Fisher: U.S. Patent 20150090874 (2015).

9) G. L. Fisher, A. L. Bruinen, N. Ogrinc Potočnik, J. S. Hammond, S. R. Bryan, P. E. Larson and R. M. A. Heeren: Anal. Chem., 88 (2016) 6433.

10) S. Iida, G. L. Fisher, J. S. Hammond, S. R. Bryan and T. Miyayama: J. Surf. Sci. Soc. Jpn., 37 (2016) 354.

11) B. W. Schueler: Microsc, Microanal. Microstruct., 3 (1992) 119.

12) NIST MS Search Program (Version 2.2).