Application Note

Complementary XPS and TOF-SIMS for Organic Analysis

Introduction

For the characterization of polymers and organic-coated surfaces, the combination of X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) can be extremely powerful. XPS provides quantitative analysis and short-range chemical bonding information from elements on the outermost surface, while TOF-SIMS provides the molecular information needed to positively identify organic species and the sub-micron spatial resolution needed to show their lateral distributions on the sample surface. Due to the additional specificity of TOF-SIMS, it can be especially helpful in situations where one or more organics are on top of another organic. Attributes for XPS and TOF-SIMS are summarized below in Table 1.

This application note describes the complementary nature of XPS and TOF-SIMS and, using two examples, demonstrates how combining the techniques is essential to more fully understand organic surfaces.

	XPS	TOF-SIMS
Probe Beam	X-rays	Ions
Analytical Signal	Electrons	Ions
Spatial Resolution	7.5 μm	0.07 μm
Sampling Depth (nm)	1-10	1-2
Detection Limits	0.1 - 0.01 at %	Ppm
Quantification	Excellent	Standards Needed
Information Content	Elemental Short Range Chemistry	Elemental Molecular
Organic Information	Yes	Yes
Depth Profiling	Yes	Yes

Table 1. Comparison of XPS and TOF-SIMS Techniques

Example 1: Contamination on Polyethylene

A quality control check using XPS on a polyethylene sheet detected trace amounts (0.3 atomic %) of O and N contamination (Fig 1). High-resolution data shows the N to be present at a binding energy consistent with N-containing organics such as amines or amides.The C spectrum (Fig 2) is predominantly hydrocarbon-based (C-C, C-H bonding), along with a very small high binding energy shoulder often associated with amide functionality (O=C-N).
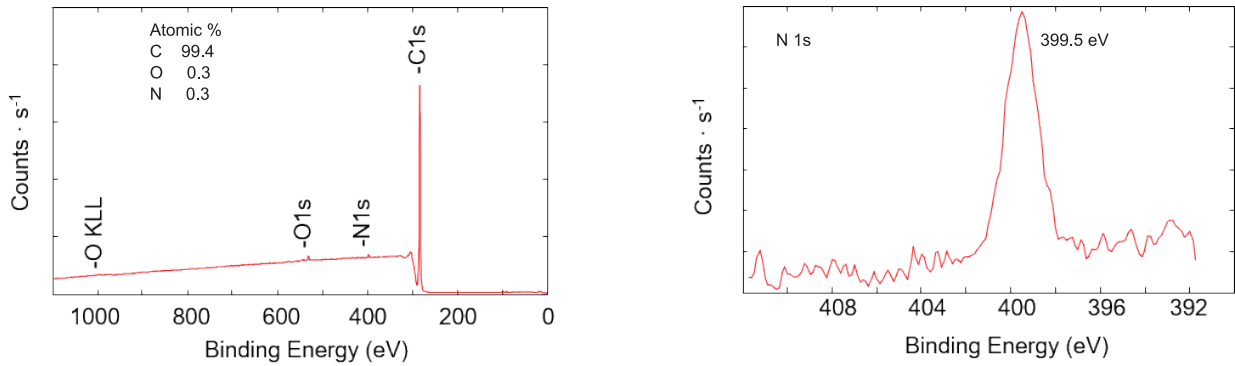
Contamination on Polyethylene (continued)

Figure 1. XPS survey spectrum and high-resolution N scan obtained from contaminated polyethylene sheet
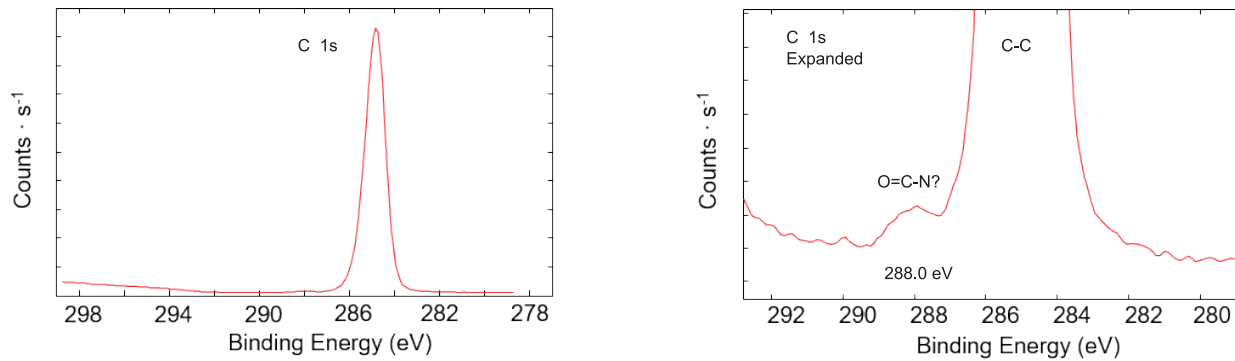
Figure 2. XPS high-resolution carbon scan of polyethylene sheet – full and expanded scales

Analysis of the same sample using TOF-SIMS showed the presence of the characteristic $C_xH_y^+$ peaks for polyethylene but also showed N-containing peaks at 72 atomic mass units (amu) ($C_3H_6NO^+$) and 338 amu ($C_{22}H_{44}NO^+$). From a TOF-SIMS spectral database search, these peaks were found to be characteristic of a common slip agent, erucamide. A comparison of the contaminated polyethylene surface to an erucamide reference spectrum is shown in Figure 3. Erucamide has a chemical formula of $C_{22}H_{43}NO$, so pure erucamide contains 4.2% N and O. Thus, even though only 0.3% N and O were detected with XPS, a good percentage of the surface carbon is actually from the hydrocarbon chain of the erucamide and not from the polyethylene.
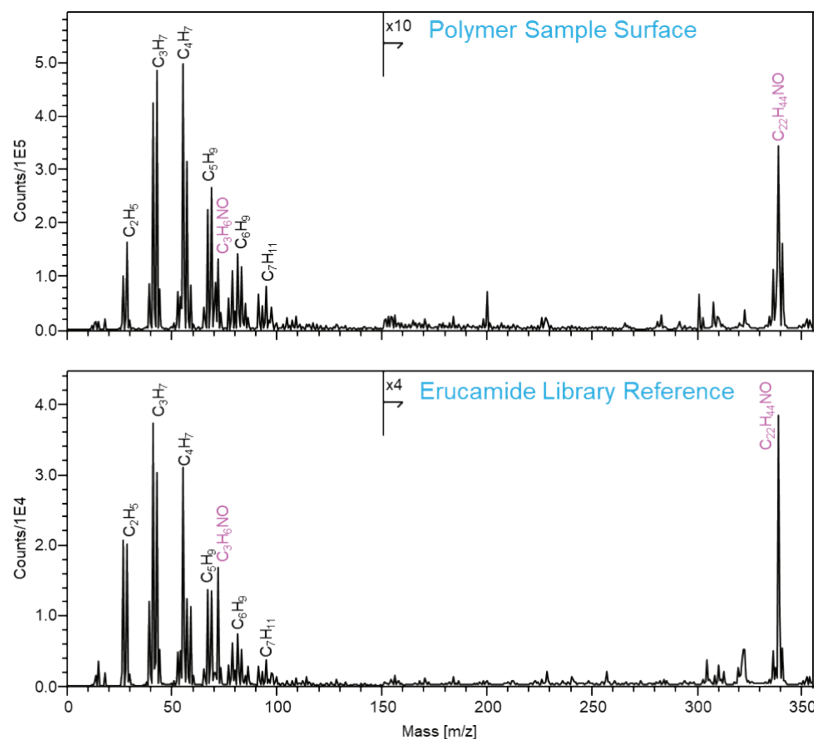
Figure 3. TOF-SIMS positive ion spectrum of the contaminated polyethylene surface compared to an erucamide reference spectrum

Example 2: Contamination on Polyethylene Terephthalate

Figure 4 shows the XPS survey spectrum of an as-received polyethylene terephthalate (PET) surface. While pure PET should contain 71% C and 29% O, this particular sample contains excess C, along with low amounts of Si, N, Na, Ca, and S.
The C high-resolution scan for pure PET should have a C-C to C-O to O-C=O peak area ratio of 3:1:1, while on this sample, it is closer to 8:1:1. So, clearly, additional C-C containing contaminants (or those overlapping C-C bonding such as Si-C from silicone) are present on the surface. The high-resolution scans for the impurity elements indicate that the N is organic-based, the S is a sulfate or sulfite, and the Si is silicone or silicate (likely silicone).
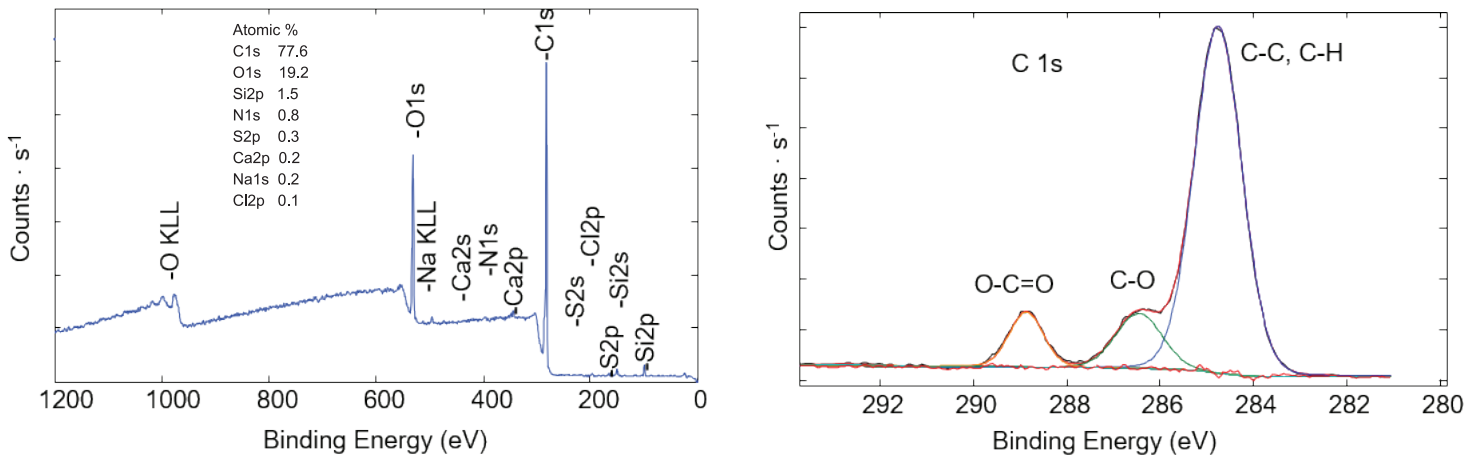

Figure 4. XPS survey spectrum and high-resolution C scan obtained from contaminated PET

For further speciation of the surface contaminants on the sample, TOF-SIMS was performed. TOF-SIMS has a surface sensitivity of 1-2 nm and excellent detection sensitivity. Thus, it provides for enhanced signal of low concentration contaminant species. Positive and negative secondary ion spectra of the PET surface are shown in Figure 5. Besides the expected peaks for PET (shown in light blue), tentative assignments were also made for polydimethylsiloxane (PDMS "silicone"), benzyl dodecyl dimethyl ammonium (BDDA), and dodecylbenzene sulfonate (DBS). To confirm the presence of these contaminants, several precursor ions observed in the TOF-SIMS spectra (MS^1) were individually deflected into a high-energy collision cell and the fragment ions were analyzed in a second TOF-SIMS analyzer (MS/MS). The MS/MS (MS^2) spectra from two precursors, tentatively assigned to BDDA and DBS secondary ions, are shown in Figure 6, along with comparisons to the matches obtained from library searches of the NIST MS/MS spectral library. The library search matches positively confirm the presence of both contaminants.
The sub-100 nm primary beam size of the TOF-SIMS provides excellent spatial resolution for determining the lateral distribution of species on the surface. Figure 7 shows secondary ion images of several contaminant peaks on the PET surface. Interestingly, the PDMS has a similar spatial distribution as the PET, while the BDDA and DBS have different distributions. The Ca distribution matches that of the DBS, indicating that the contaminant may be the Ca salt of DBS.
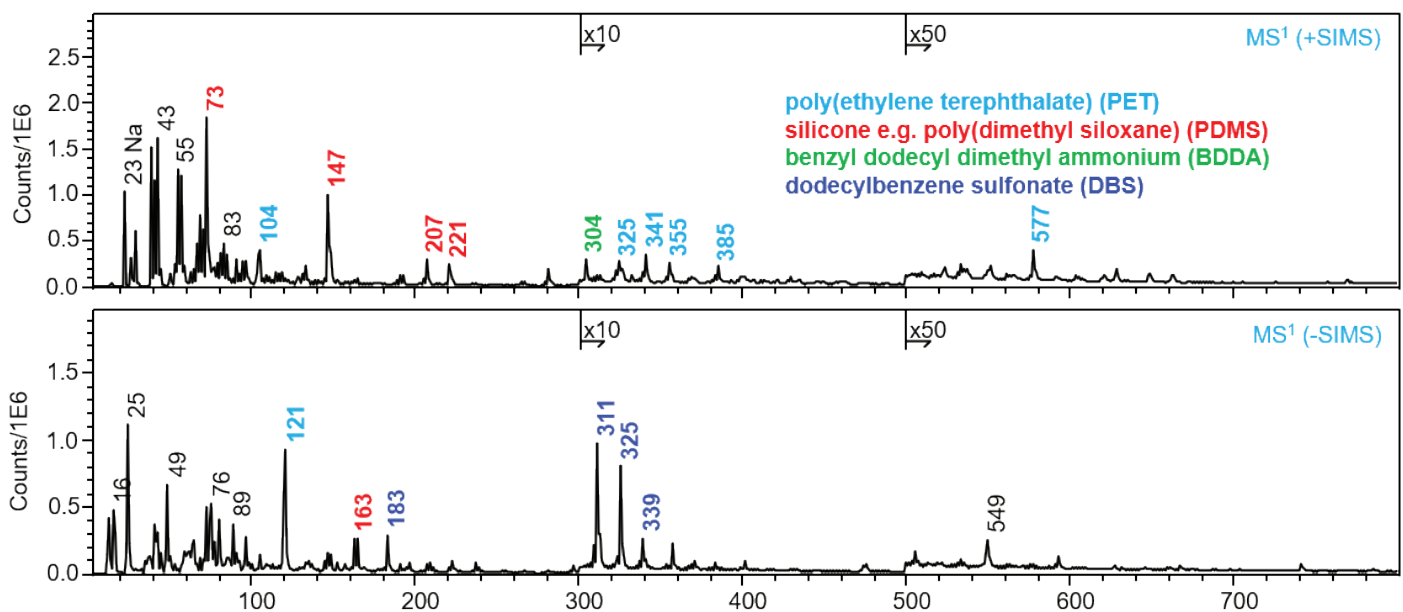

Figure 5. TOF-SIMS positive and negative secondary ion spectra of the contaminated PET surface

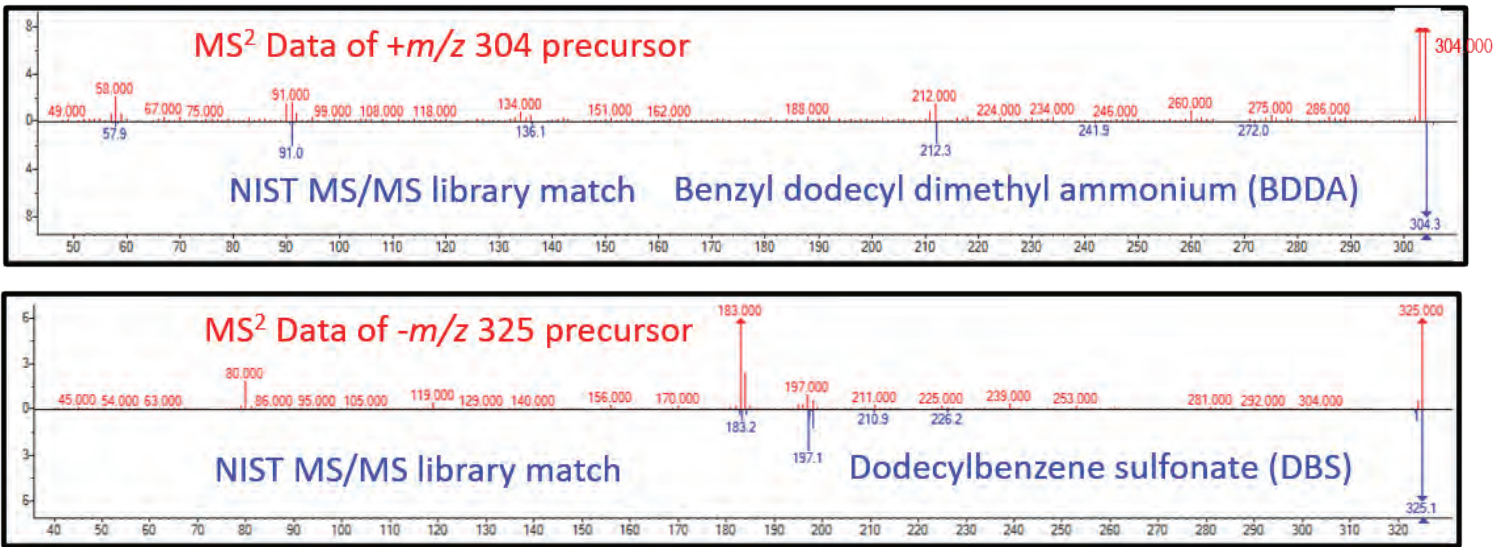# Example 2: Contamination on Polyethylene Terephthalate (continued)

Figure 6. TOF-SIMS MS² spectra (in red) for precursor ions observed on the PET surface, tentatively assigned as BDDA and DBS, compared to the NIST MS/MS library search matches (blue spectra). The library search matches confirm the presence of both contaminants. Note that more thorough fragmentation of the parent ion is observed using PHI's high-energy collision cell compared to the database's low energy collision cell data.

PET $C_7H_4O^+$ (+m/z 104)   PDMS $C_7H_{21}Si_3O_2^+$ (+m/z 221) Ca^+ (+m/z 40)   BDDA $[M]^+$ (+m/z 304)

PET $C_7H_5O_2^-$ (-m/z 121)   PDMS fragment (-m/z 163)   DBS fragment (-m/z 183)   DBS SO_3^- (-m/z 80)
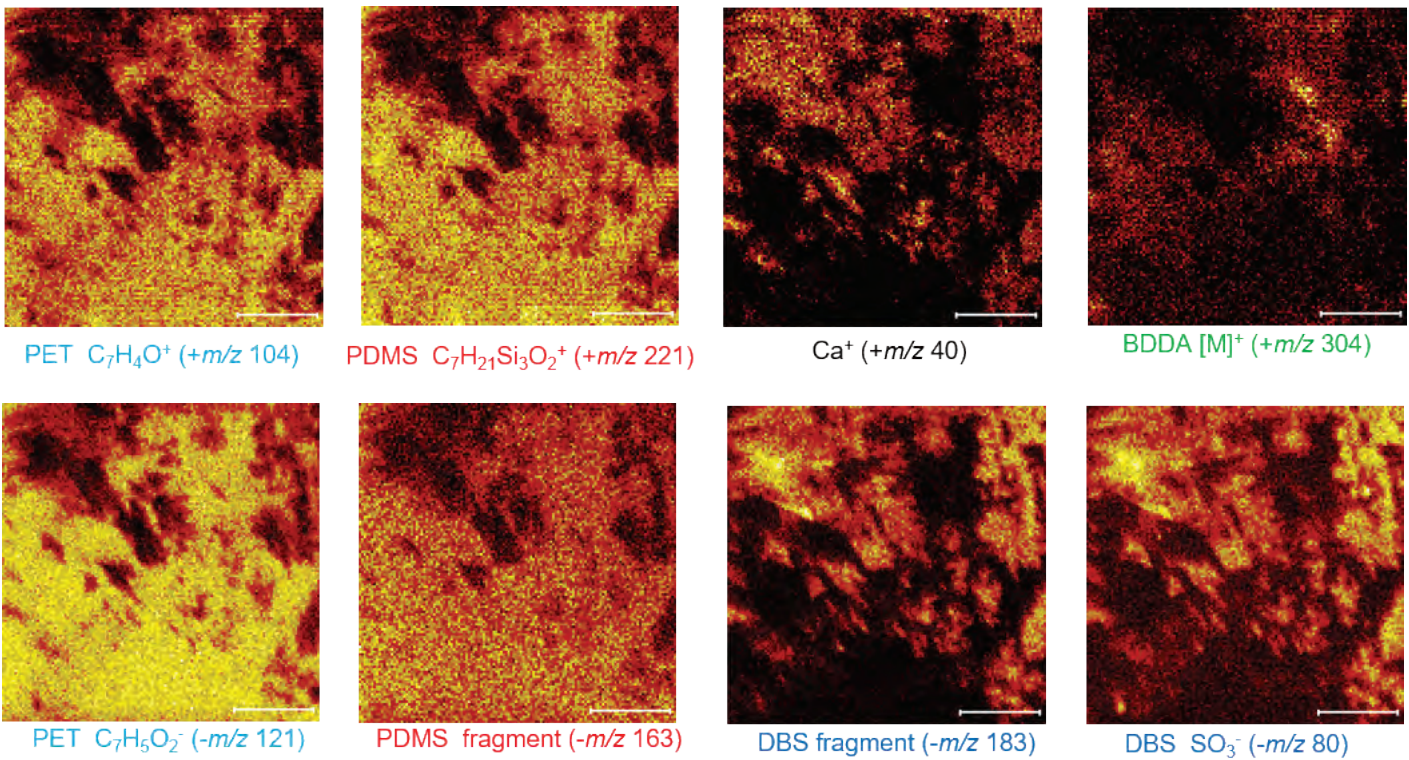
Figure 7. TOF-SIMS positive and negative secondary ion images showing the lateral distribution of Ca, PDMS, BDDA, and DBS contaminants on the PET substrate. Each image has a field of view of 400 μm (scale marker is 100 μm).

Summary

These two examples very clearly show the complementary nature of XPS and TOF-SIMS for studying contaminated organic surfaces. XPS can quantify the amount of contamination present and provide information on the chemical states of the elements detected, while TOF-SIMS provides the molecular information needed to positively identify organic species and the spatial resolution needed to show their lateral distributions on the sample surface.