Time of Flight- Secondary Ion Mass Spectrometry (TOF-SIMS)

Why should I use TOF-SIMS and why is it important?

- Identification of the molecules present on the surface of a sample, surface chemistry identification.
- Detection limits are typically from ppm to ppb
- High mass resolution (minimum two decimal place mass accuracy).
- Variable depth-can be used to penetrate angstroms to multiple nanometers deep.

How does TOF-SIMS work?

TOF-SIMS is a mass spectrometry technique in which a solid sample is bombarded by ions, which then release fragments of the surface molecules. The material ejected from the sample typically is from only the first few atomic layers. The depth of penetration depends on the initial energy (KeV) imparted to the primary ions. A general diagram of this effect can be seen below in **Figure 1**. The impact of the primary ions with the sample surface causes fragmentation and ejection of the molecules on the immediate surface. As with most mass spectrometry techniques, molecules fragment resulting in a characteristic pattern which can be used for identification. The exact amount of fragmentation is dependent on the KeV of the primary ions used. If a low enough KeV is used, molecules can be ejected with very low amounts of fragmentation, even up to 10,000 Atomic Mass Units (amu). These fragments are then analyzed in the time of flight mass spectrometer. The KeV can also be tuned to cause ejection of specific ions in a sample at a specific depth, and can thus additionally be used for depth profiling experiments. These experiments typically identify individual elements or low molecular weight ions, as large ions tend to be unable to penetrate the surface from a depth of multiple nanometers.
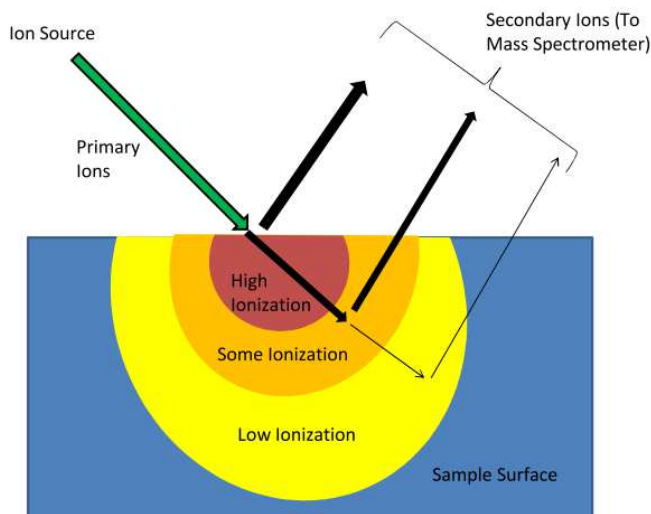
Sample Preparation and Introduction: Samples are generally analyzed as received. Sample modification or preparation tends to leave detectable residues, which are not ideal when conducting an analysis of the surface chemistry of the sample. The sample is usually gently cleaned with nitrogen immediately before analysis to remove contaminants, although it is not a required step. Small particulate samples can be placed on indium foil, which creates a conductive surface to highlight the particles being analyzed. Areas analyzed can be as small as 0.2 µm, the size of the probe, and as large as 200 mm.

Figure 1: Diagram of Ion Impact and Ejection from Sample Surface

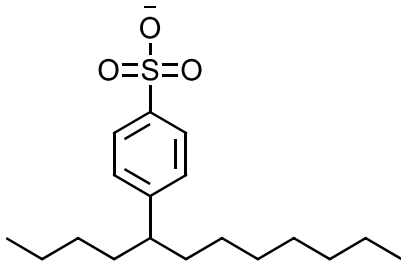## Applications of TOF-SIMS: Understanding Sample Slipping

Figure 2: 4-(5-Dodecyl) benzenesulfonate

TOF-SIMS excels at identifying surface chemistry as compared to bulk chemistry, and can therefore provide insight regarding the surface layer and how slip properties arise in a material. **Figures 3-4** show acquired data in positive and negative ion modes respectively for a sample that was exhibiting good slip characteristics. The sample was a polydimethylsiloxane. The spectrum shows that the surface layer on the good sample is composed primarily of hydrocarbons including aromatic components. In **Figure 4,** the negative ion mode spectrum shows signals consistent with a surfactant. A common surfactant that is consistent with the fragmentation patterns observed is 4-(5-Dodecyl) benzenesulfonate (**Figure 2**). Analysis of a control sample with poor slip properties did not show these hydrocarbon components. Further analysis of this sample could include surface mapping of the sample using TOF-SIMS. Surface mapping shows the location of a particular chemical component (ion distribution). An example would be searching the spectra for 127 and 265 to identify the presence of 4-(5-Dodecyl) benzenesulfonate across the entire surface of the sample. This can be performed for multiple ions, and therefore multiple compounds on a single sample.
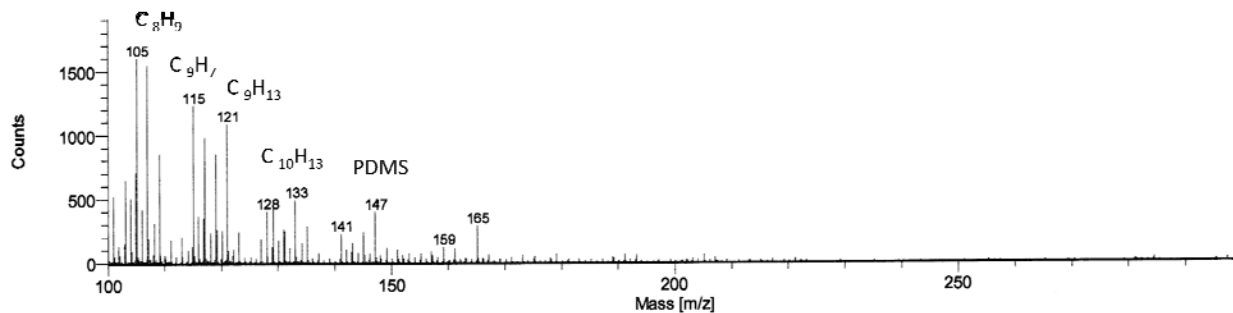

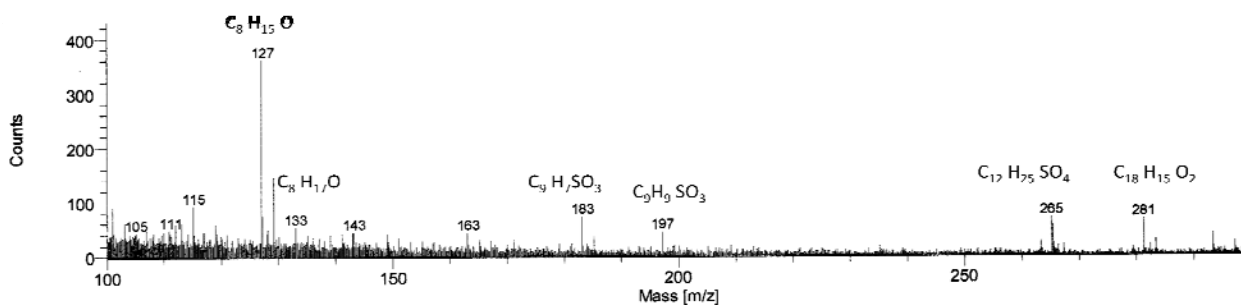**Figure 3**: *Time of Flight Mass Spectrum, Positive Ion Mode*

Figure 4: *Time of Flight Mass Spectrum, Negative Ion Mode*