# Additive Identification using TOF-SIMS Parallel Imaging MS/MS

## Introduction

A challenge with traditional TOF-SIMS analyses is that the composition of high mass fragments (>200 daltons) can sometimes be difficult to unambiguously identify. Due to the large number of elemental combinations possible to produce a given nominal mass, even milli-mass unit mass accuracy and mass resolution of ~15,000 m/$\Delta$m are often insufficient to positively identify the molecular fragmentations and elemental composition of high mass peaks. Now, with the use of a TOF-SIMS parallel imaging MS/MS instrument [1,2], peaks of interest can be selected, fragmented, and mass analyzed to uniquely identify their composition. This application note shows the usefulness of a TOF-SIMS parallel imaging MS/MS instrument for determining the composition of an unknown additive on the surface of a multi-component mixture.

## Experimental

In a traditional TOF-SIMS analysis, the secondary ions generated from the sample surface are extracted and mass (time-of-flight) separated as they traverse through the spectrometer. A pulse counting detector (MS1) is used to count these secondary ions and a full mass spectrum is collected for each image pixel. In the MS/MS mode, the precursor ion of choice is deflected into a high energy collision induced dissociation (CID) cell. In the CID cell, the precursor ions collide with argon gas atoms resulting in fragmentation of the precursor ions. The fragment ions are mass separated in a linear TOF analyzer and counted at a second pulse counting detector (MS2) while the rest of the ions are collected as usual with the MS1 detector (Figure 1). Again, with the MS2 detector, a full mass spectrum is collected at high speed for each image pixel.
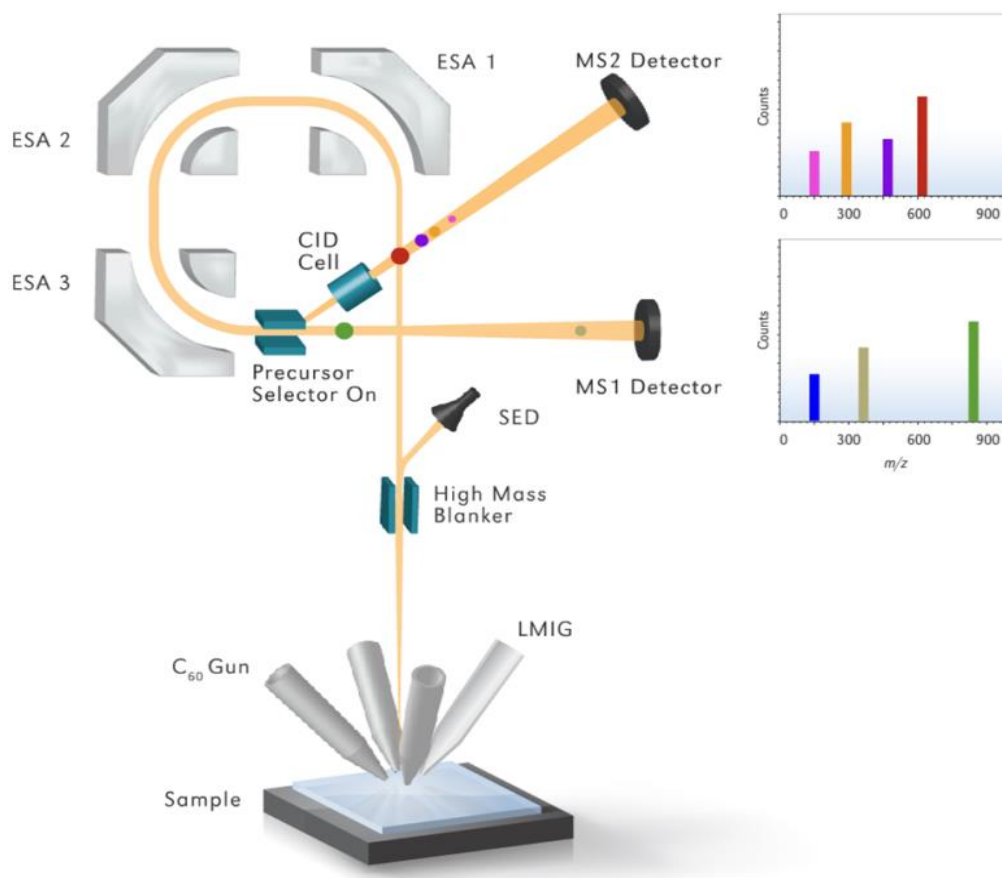


*Figure 1. Diagram of TOF-SIMS Parallel Imaging MS/MS Instrument*

## Results

TOF-SIMS analysis of a complex mixture on a proprietary material showed the presence of an unknown peak at 201 m/z in the negative ion polarity, believed to be an additive in the material. To help determine the composition of the additive, the 201 peak was selected as the precursor ion and deflected into the high energy CID cell. Figure 2 shows the mass spectrum (MS$^2$) of the ions exiting the CID cell. The top spectrum is displayed in mass-to-charge ratio (m/z) while the bottom spectrum shows the mass loss of each ion relative to the precursor ion. After identifying some of the lower-mass peaks, the spectral mass calibration was updated and additional peak assignments were made using knowledge obtained from the lower mass fragments. Figure 3 shows an example of the assignment process of the mass 93 peak. The composition of other fragments must also be taken into consideration in making plausible assignments. The composition assignments for all of the masses observed in the MS$^2$ spectrum, along with the proposed structure of the precursor ion (diphenylphosphine oxide - DPPO), are shown in Figure 4. Select mass fragments (47, 77, and 124 m/z) originating from the DPPO structure are also shown. A literature search of DPPO indicates that it can be used as a photo-initiator, making perfect sense as an additive in the complex proprietary material.

## Summary

This work demonstrates the application of TOF-SIMS parallel imaging MS/MS for identifying an unknown component of a multi-component mixture. Being able to confidently identify the composition of unknown peaks brings TOF-SIMS analysis to a totally new level of sophistication and usefulness.
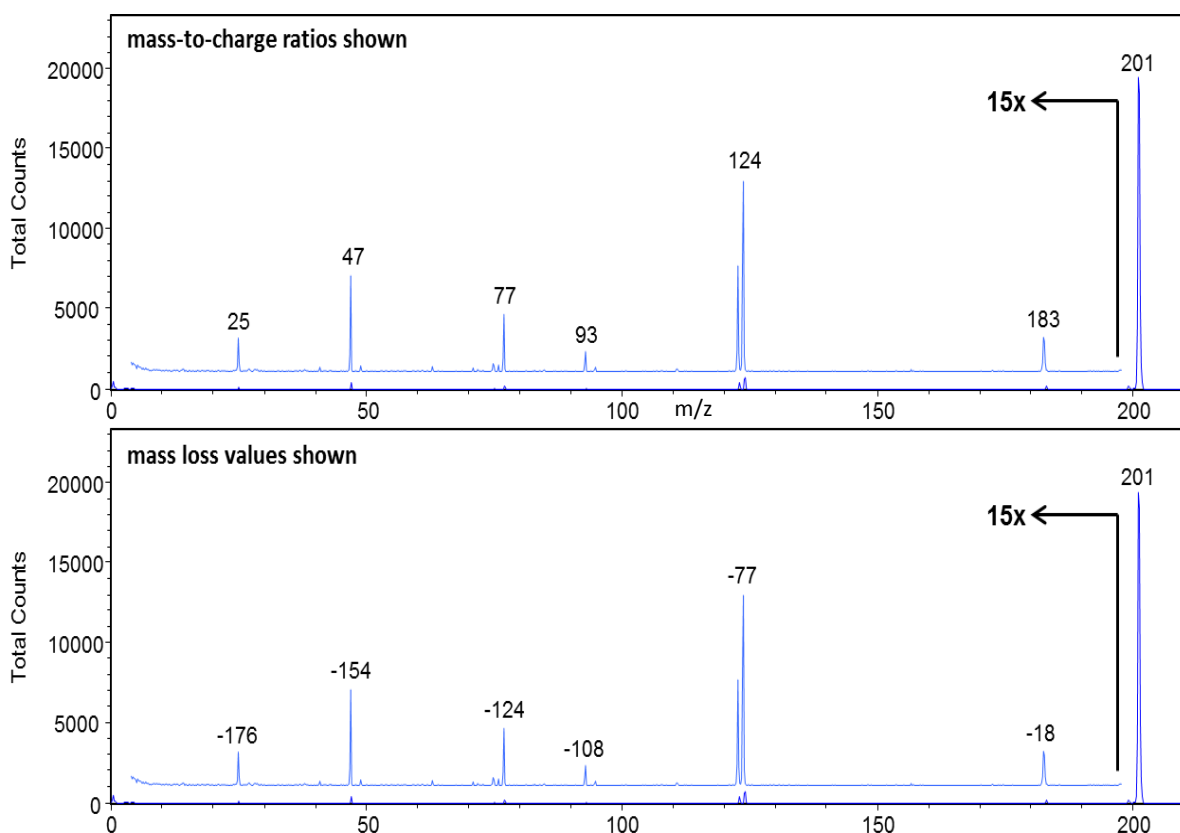


Figure 2. Negative secondary ion mass spectrum of ions exiting the CID cell (precursor selector set to 201 m/z) and collected at the MS2 detector. The top spectrum has the peaks labeled in m/z while the bottom spectrum shows the mass loss of each ion, relative to the 201 m/z precursor ion.
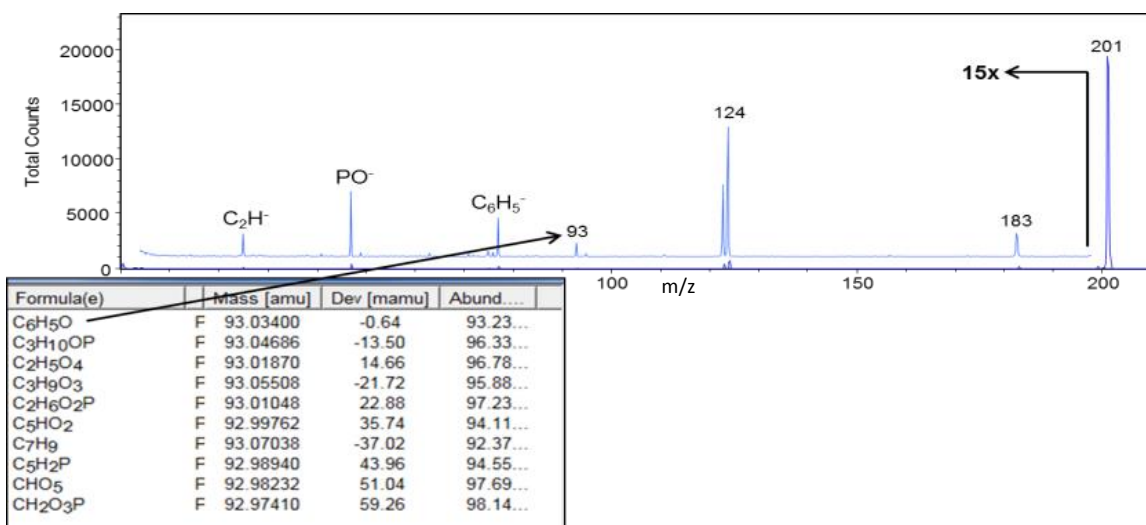
Figure 3.  MS$^2$ negative fragment ion spectrum of the 201 m/z precursor peak showing low mass assignments and compositional assignment of mass 93 using the Peak ID function.
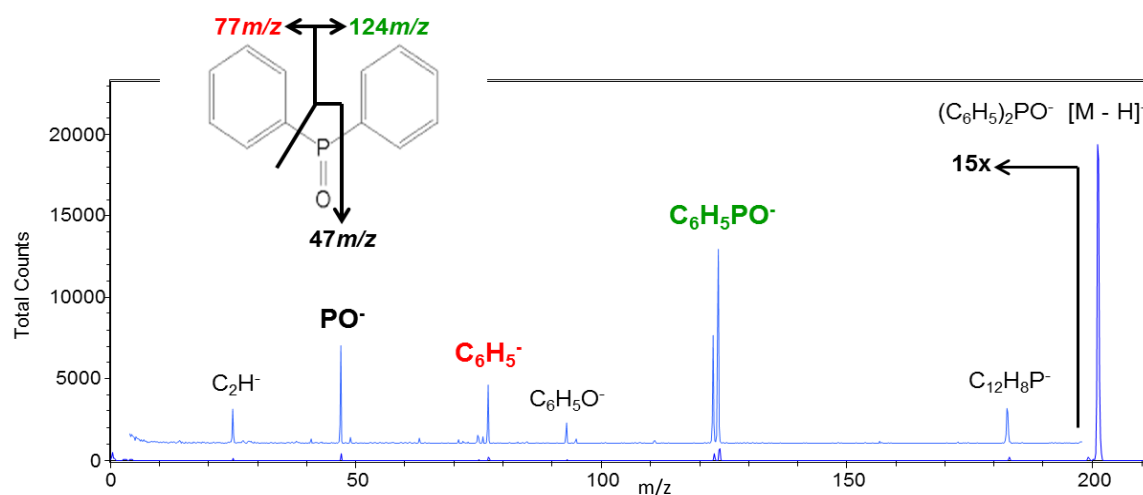


Figure 4.  Peak assignments for the MS$^2$ negative ion spectrum of the CID fragments from the 201 m/z precursor peak.  The precursor peak is identified as diphenylphosphine oxide; its structure and select mass fragments are shown in the insert.

## References

1.  US patent granted; Japan and EU patents pending

2.  Bryan, S., Fisher, G., Hammond, J., Larson, P., (2015, September), New Instrument with Parallel TOF-SIMS and MS/MS Data Acquisition, Paper presented at the SIMS XX meeting, Seattle, WA.