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Direct Analysis in Real Time (DART) Ion Trap Mass Spectrometry for Detection and Identification of poly(dimethylsiloxane) Polymers on Surfaces

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Overview

Purpose:
- **Determine if DART analysis is useful for detecting nonpolar PDMS species**
- **Develop rapid peak identification methods for comparing samples**
- **Measure effects of baking procedures intended to remove mold release formulations**

Methods:
- **DART (direct analysis in real time) ionization with Ion Trap Mass Spectrometry**
- **Deposit diluted known standards and commercial mold release formulations on glass**
- **Peak detection methods using Matlab**

Results:
- **Non-polar trimethylsilyl terminated and other terminated PDMS can be detected**
- **PDMS baking procedures reduce but also spread PDMS on surface**
- **Simplified peak detection methods show promise but need additional development**

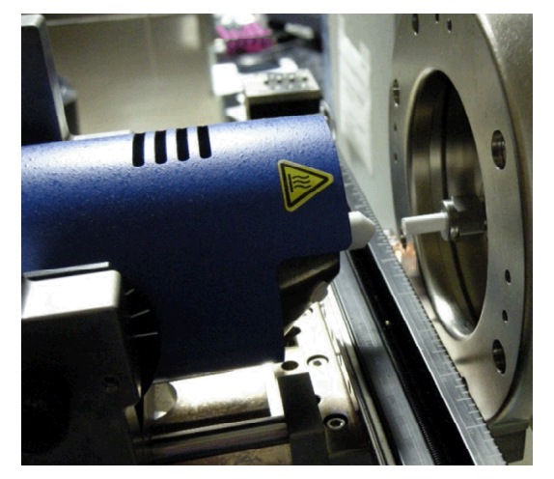
Introduction

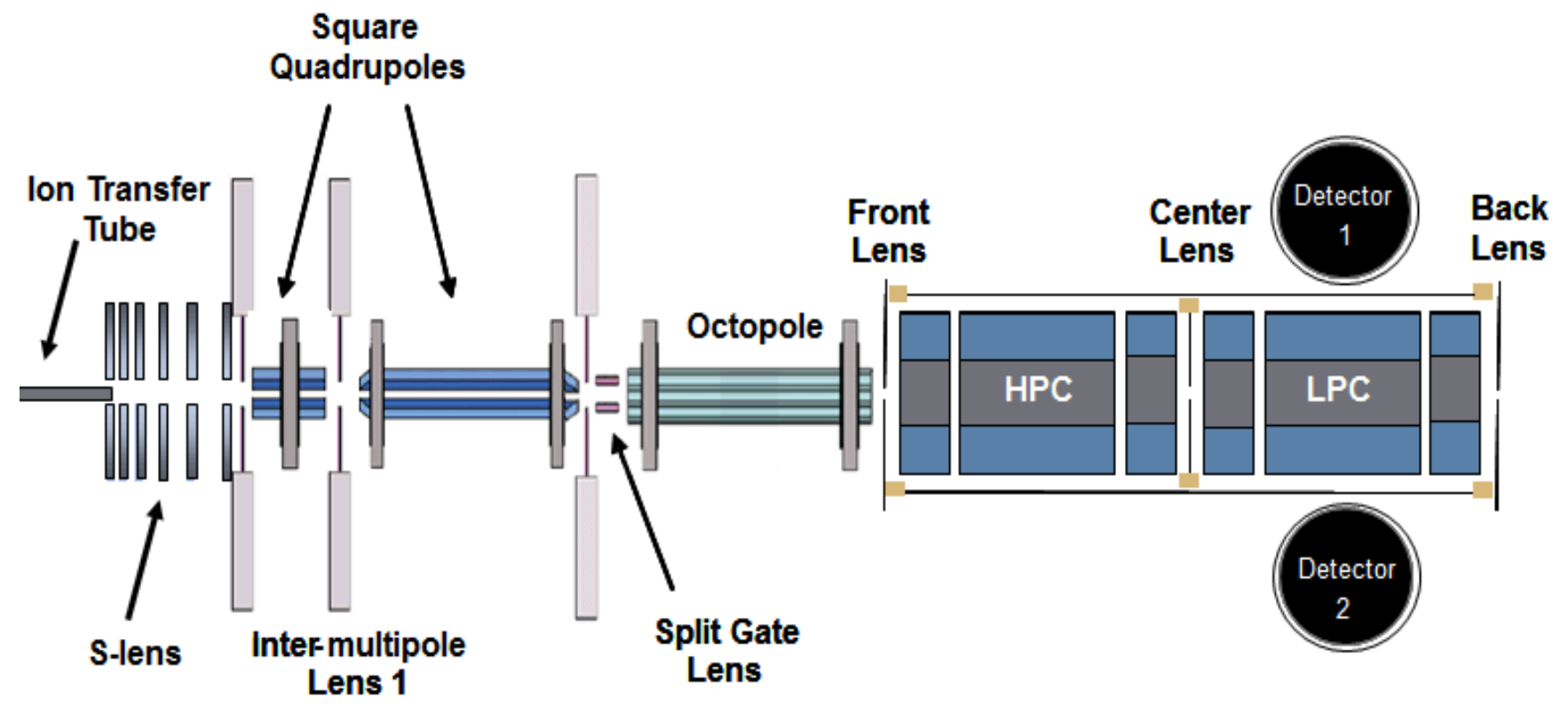
Mold release formulations are used in a variety of industrial settings to prevent adhesion or act as a barrier. They consist of polymers that become the barrier and solvents which help distribute the polymer. Common mold releases use poly(dimethylsiloxane) oligomers of various weight ranges depending on the application. In some precision applications there is concern that mold release constituents are not fully removed during processing or curing, or that decomposition or reactivity prevents complete removal. Reactive constituents or decomposition may lead to undesirable materials remaining on parts or transferring to other parts during processing. Direct analysis in real time (DART) allows us to monitor *in situ* the residual components and/or decomposition products of mold release on materials.

Methods

Ambient ionization (DART) in Helium mode allows rapid analysis of non-polar siloxane polymers and products.

DART ion source





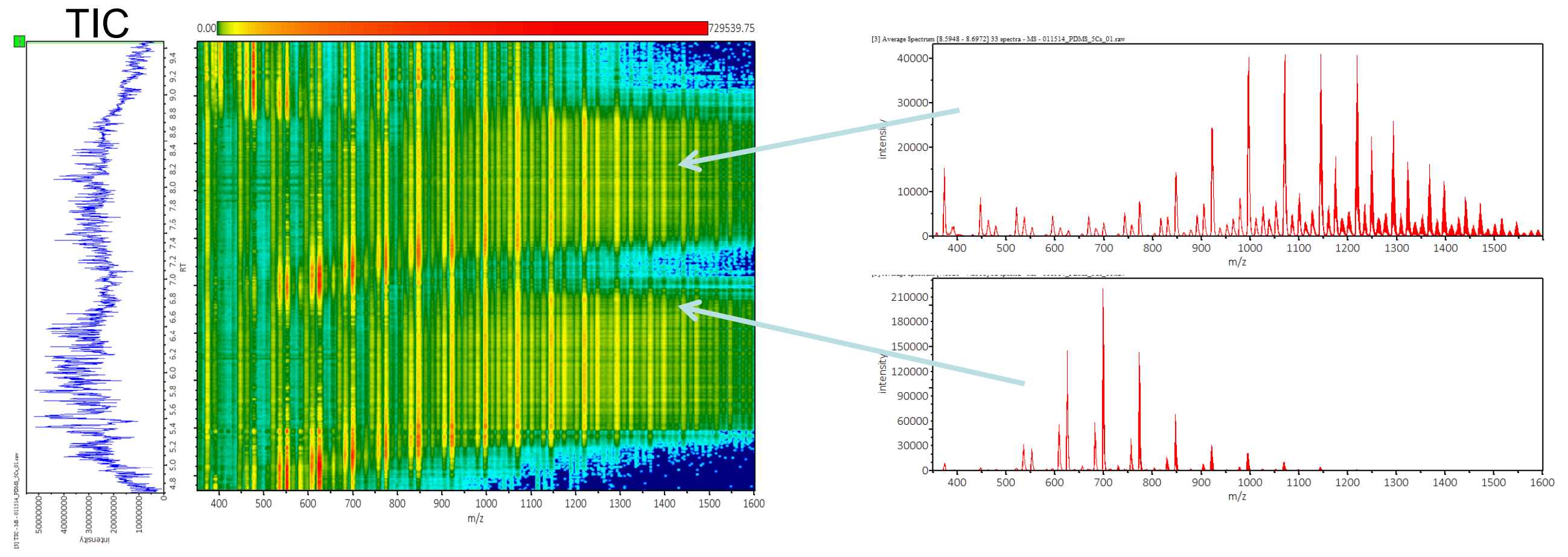
MS^N with Ion Trap Mass Spectrometer.

Trimethylsilyl terminated PDMS standards (termination confirmed by NMR) with viscosity from 5cS to 50cS were diluted to less than 20mg/mL in hexane and deposited (approx. 2 microliters) on glass slides or “dip it” tubes. A linear rail moved the sample across the active zone of the DART at a speed of 0.2 mm/minute. No dopants were added.

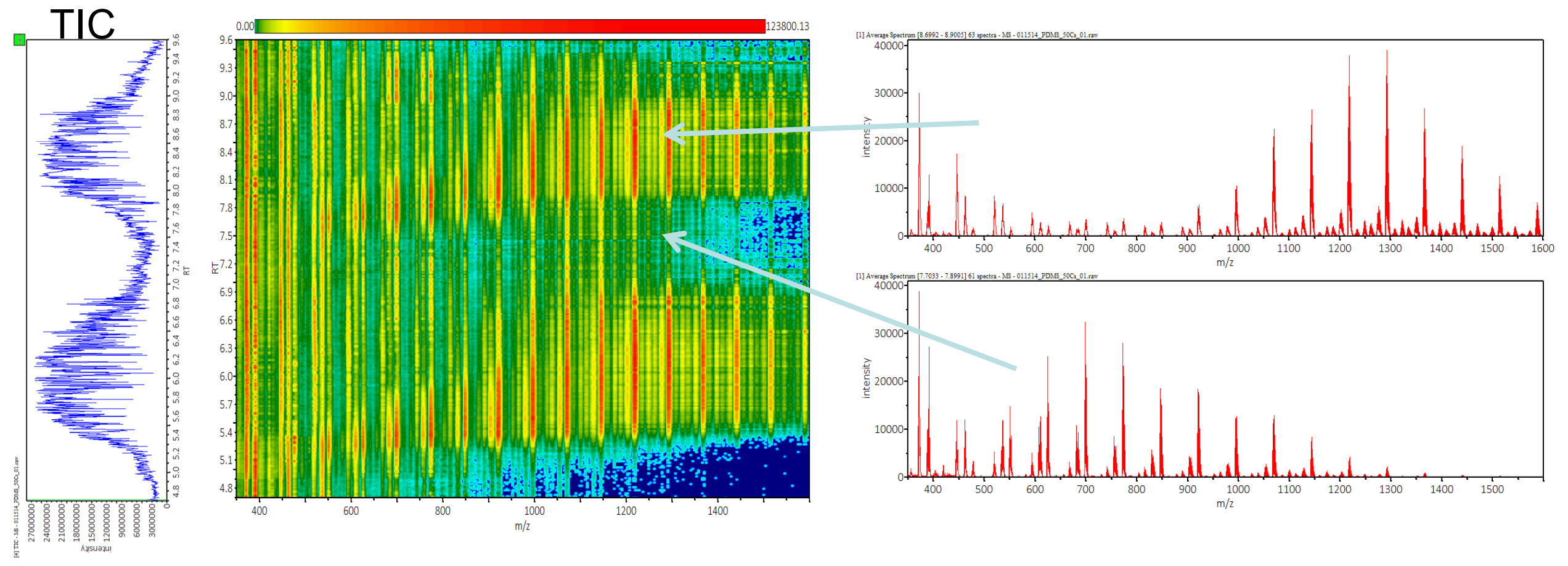
Results

The total ion current (TIC), heatmap plot (m/z signal versus time versus color intensity), and individual m/z spectra show possible thermal effect as glass slide heats up as DART rasters across glass slide. $[M+NH_4]^+$ were observed as described previously [1].

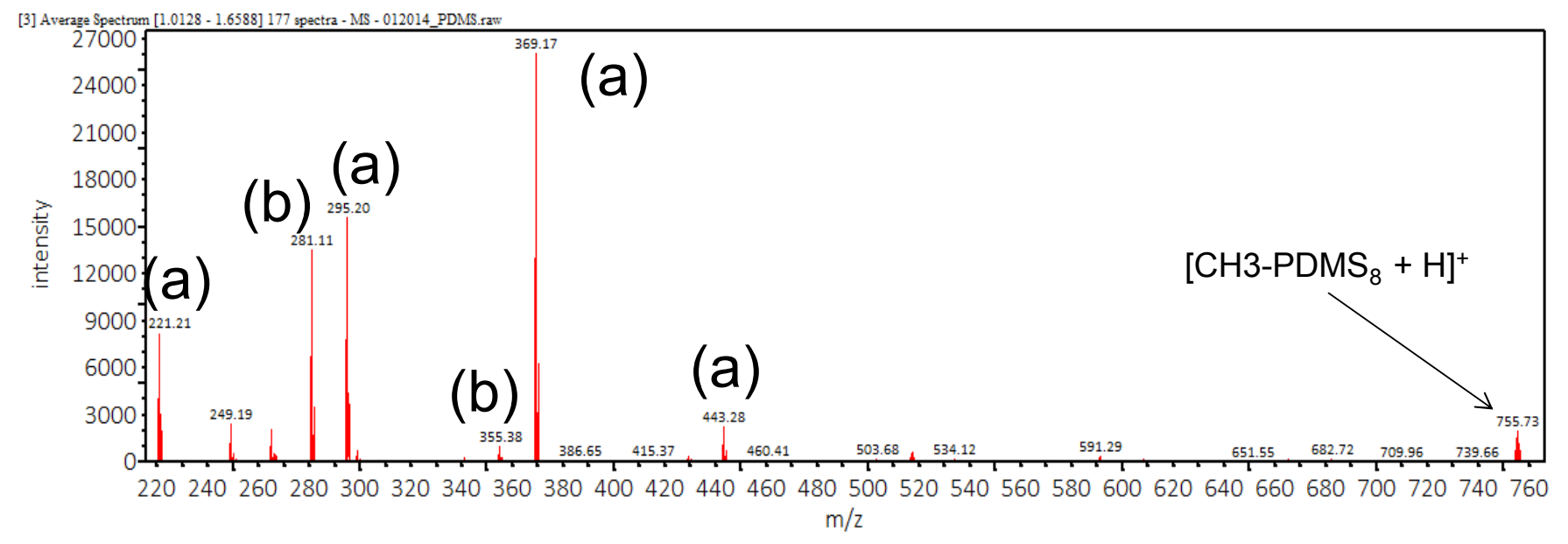
PDMS 5cS



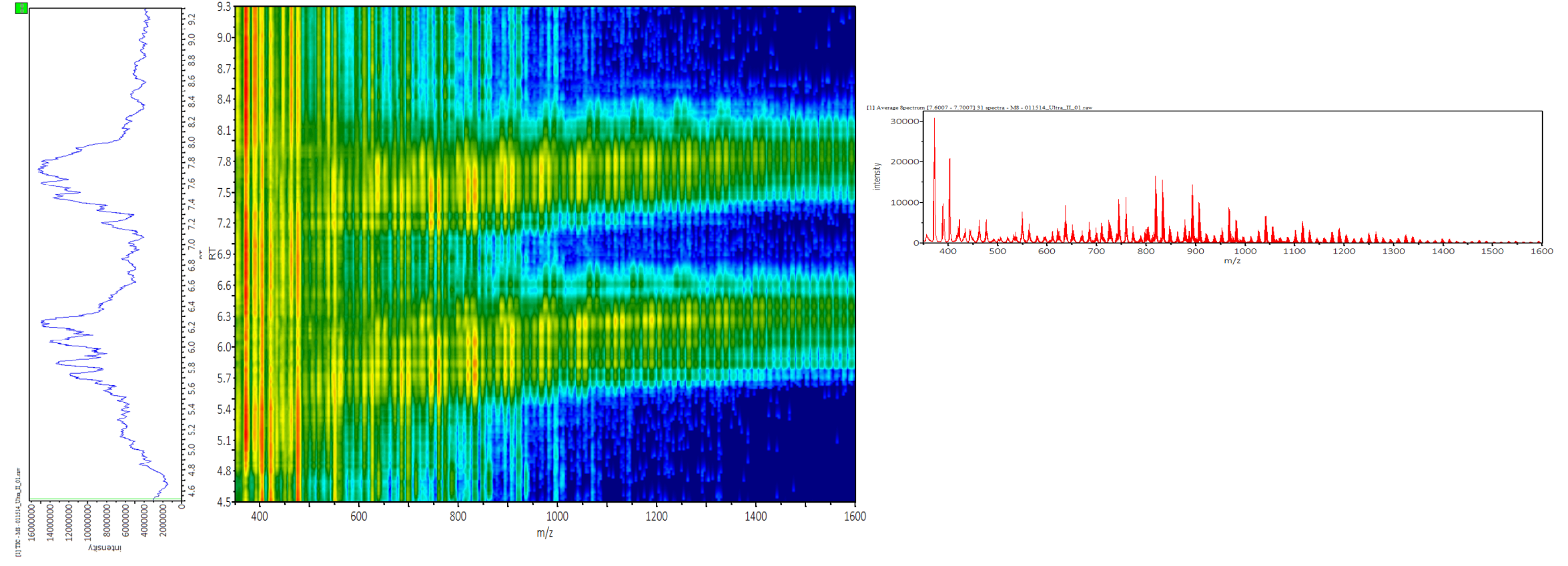
PDMS 50cS



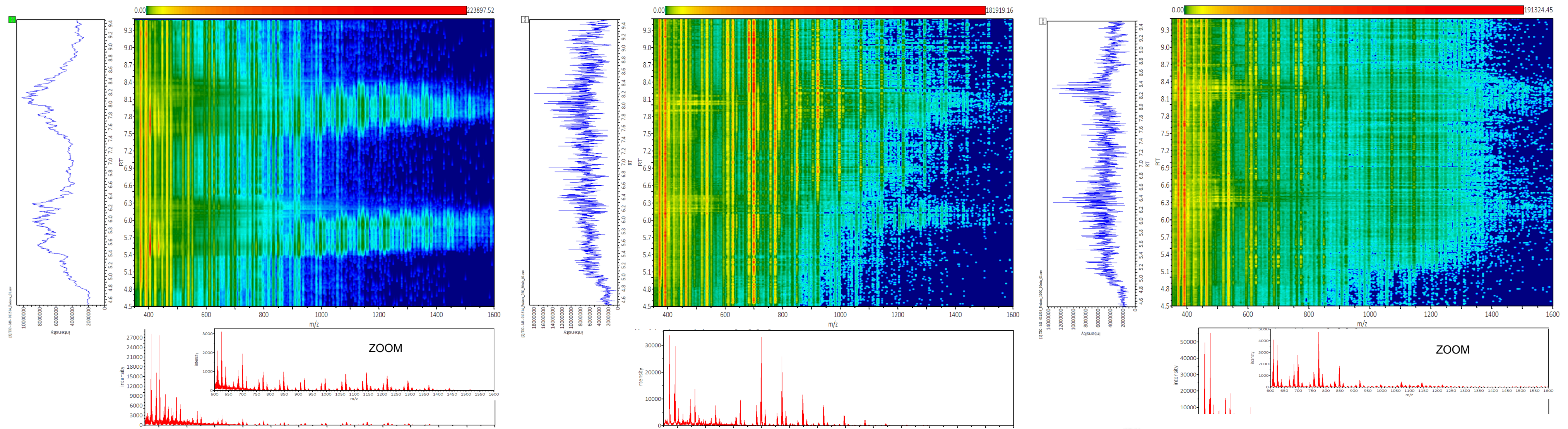
MS/MS of TMS-PDMS$_8$ (m/z 772) shows both (a) Rn+73, (b) Rn+55 ions as in reported electrospray adducts [2].



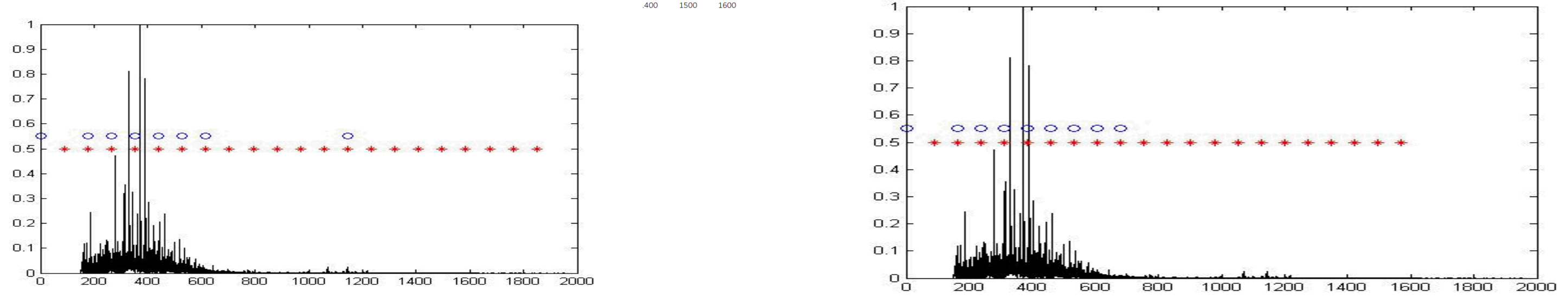
Peaks were detected in mold release commercial formulation #2 corresponding to hydroxyl-terminated and TMS-terminated.



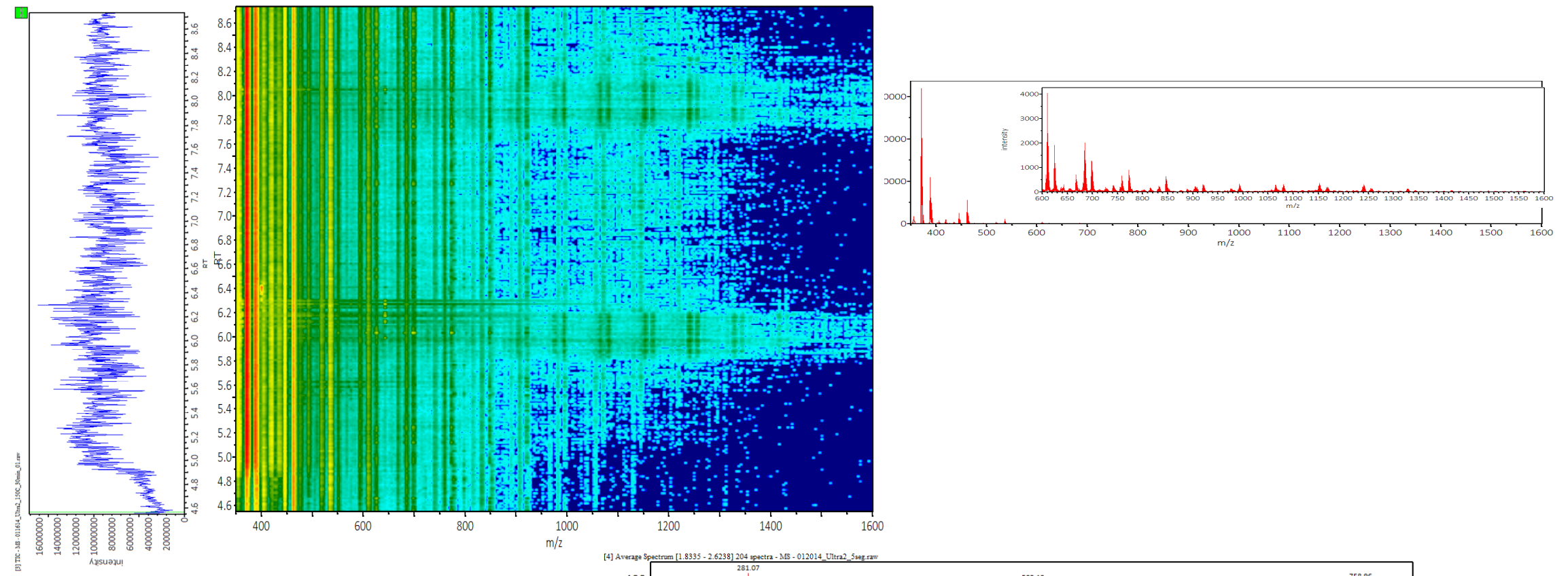
Heat treatment of mold release (formulation 1) shows spreading and changes in detected distribution (no heat, 75C, 100C.)



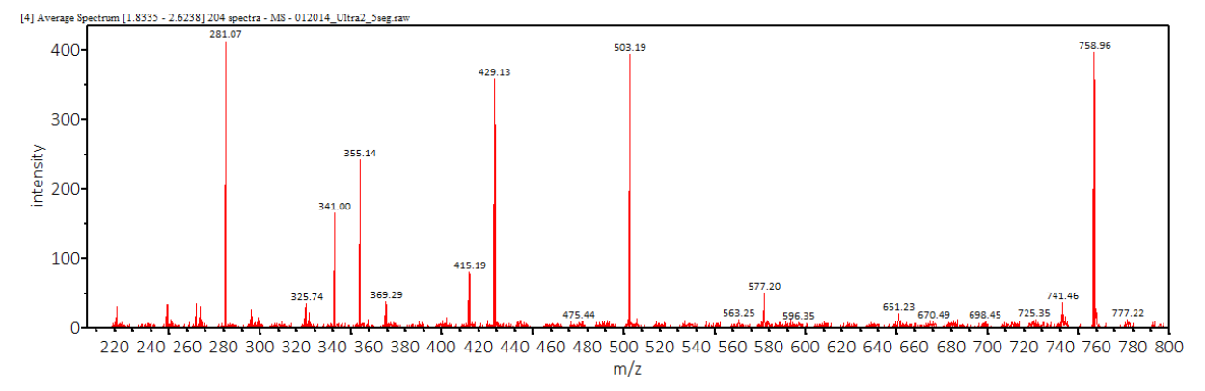
Matlab peak matching shows ethyl (left) and methyl (right) variants of PDMS detected in formulation #1 after 100C treatment.



150°C 30 min.
Increase in low m.w. cyclic silanes.



MS/MS of cyclic silane m/z 758 yields more Rn+55 fragments.



Conclusions

Trimethylsilyl-terminated PDMS and other terminated PDMS in commercial mold release formulations can be detected by DART-MS as the ammonium adducts. Baking methods employed for mold release removal result in spreading but also a decrease in coverage, as expected. An increase in the signal from low molecular weight cyclic silanes was observed with increasing heat treatment. DART analysis has a thermal effect not unexpected on spot surfaces – raster rate and time-on-sample can effect signal thus average m.w. observed. MS/MS fragments confirmed termination of different oligomers. Based on this basic work, DART is proving useful for the detection of mold release agents on actual parts for the optimization of removal techniques and contamination detection.

References

1. Bridoux, M. C.; Machuron-Mandard, X., Capabilities and limitations of direct analysis in real time orbitrap mass spectrometry and tandem mass spectrometry for the analysis of synthetic and natural polymers. *Rapid Commun. Mass Spectrom.* **2013,** *27* (18), 2057-2070.
2. Fouquet, T.; Humbel, S.; Charles, L., Tandem Mass Spectrometry of Trimethylsilyl-Terminated Poly(Dimethylsiloxane) Ammonium Adducts Generated by Electrospray Ionization. *J. Am. Soc. Mass Spectrom.* **2011,** *22* (4), 649-658.

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