Analysis of Additives in a Polyethylene Storage Bag by Using the Q1500 Direct Insertion Probe

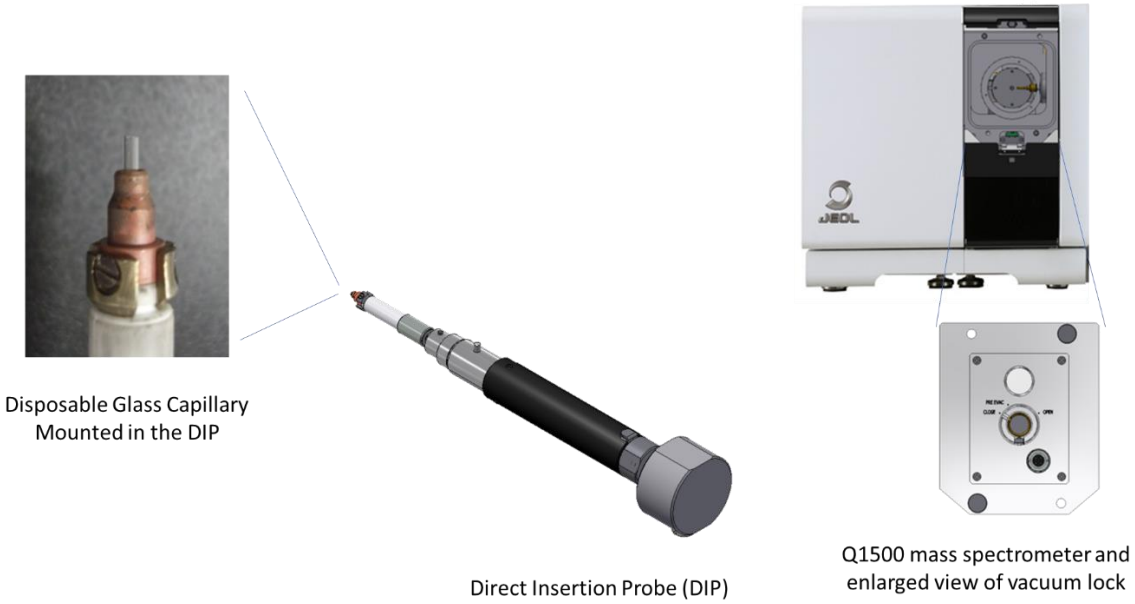
Product: JMS-Q1500GC MS System

Introduction

The Direct Insertion Probe (DIP) option permits rapid analysis of solid or liquid samples without gas chromatography. Samples contained in a disposable glass capillary are introduced with the DIP directly into the Q1500 ion source through a vacuum lock. The DIP temperature can be programmed for fast or slow heating to desorb or pyrolyze samples for analysis. In this example, we use the DIP to detect additives in a low-density polyethylene storage bag.

Experimental

Scissors were used to cut a small piece (approximately 1mm x 0.5 mm) from a corner of the plastic bag. The solid sample was introduced into a glass capillary (2 mm O.D.), which was then inserted into the DIP.

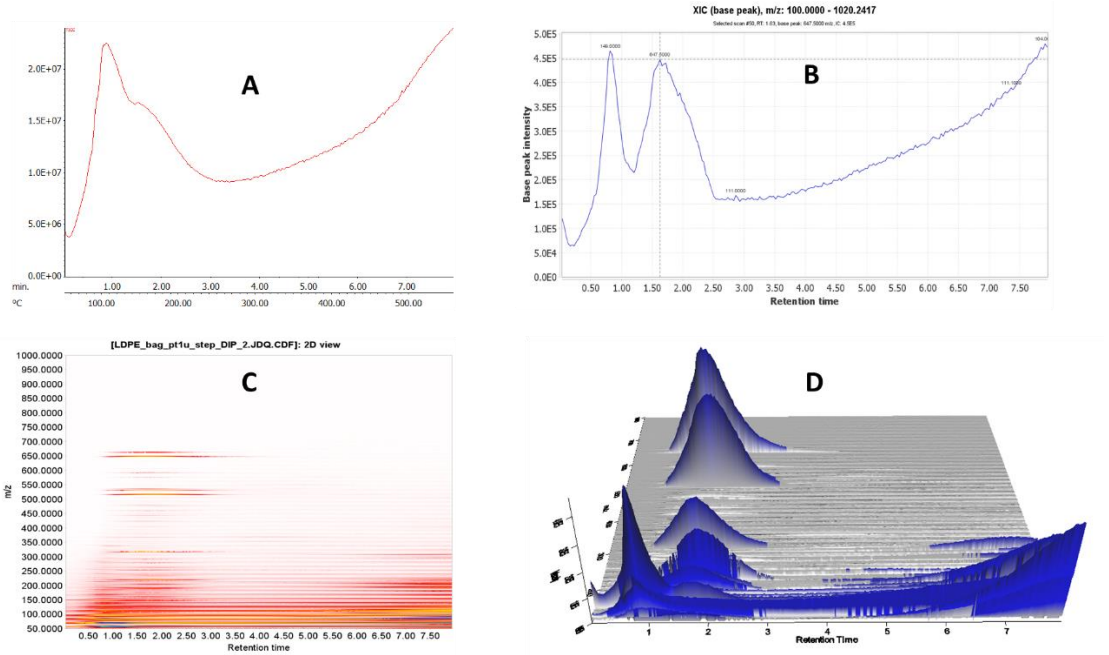


The Q1500GC Direct Insertion Probe (DIP) and Vacuum Flange

After inserting the DIP into the mass spectrometer through the vacuum lock, the sample was heated from 50°C to 500°C at a rate of 64°C min^{-1} and held at 500°C for 2 minutes. Mass spectra were acquired for the range *m/z* 35 to *m/z* 1000 at a spectral acquisition rate of approximately 1 spectrum per second and a *m/z* step size of 0.1. Data were analyzed using the Data Reduction function in the *Escrime* software of the Q1500GC data system. Data were exported from *Escrime* in netCDF format for visualization with base peak chromatograms, 2D graphs, and 3D graphs with the open source *mzMine2* program[1].

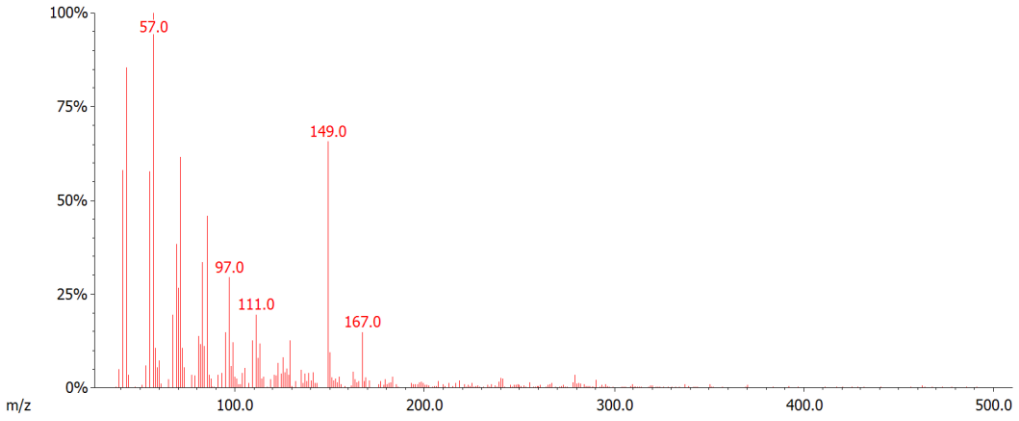
Results

The total ion current chromatogram (TICC) shows increases in ion current in the temperature range from approximately 100-250°C and a gradual increase in current from 300-500°C. The base peak chromatogram and 2D and 3D graphs show that the most intense peak above *m/z* 100 at around 100°C is *m/z* 149, and that the most intense peak at around 150°C is *m/z* 647.5. At higher temperatures, we see an increase in the alkyl peaks from pyrolysis of the polyethylene.

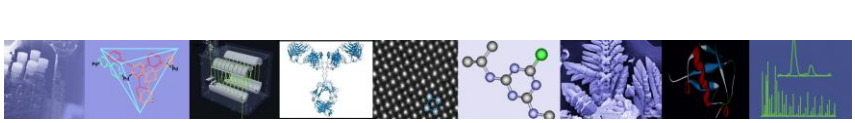


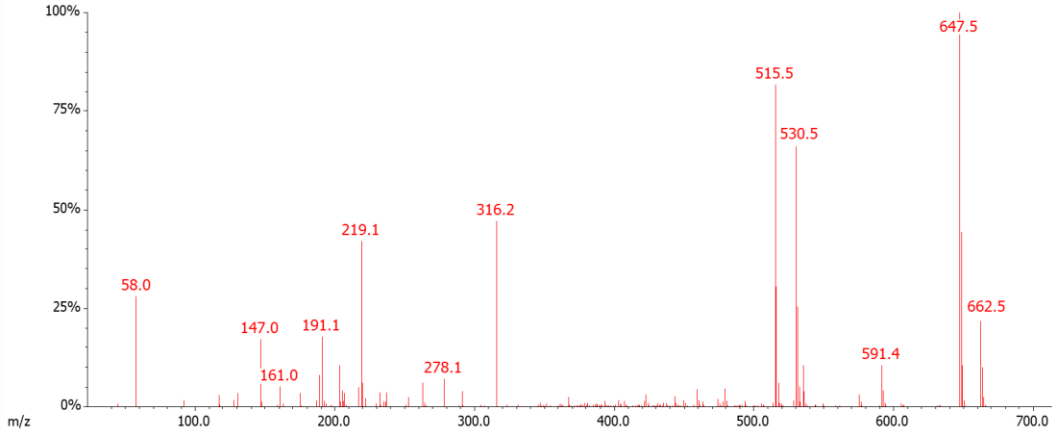
Different ways to visualize the time and temperature dependence of compounds
A: Total ion current (TIC), B: Base peak chromatogram, C: 2D graph, D: 3D graph.

Around 100C, we can see the familiar phthalate fragments at *m/z* 149 and *m/z* 167 and alkyl fragments from the polyethylene. We cannot conclusively identify which phthalate is present from this spectrum because of the high alkyl background and the fact that phthalates do not produce molecular ions in electron ionization (EI) mass spectra, but the compound was identified by other means (AccuTOF-DART) as bis(ethylhexyl) phthalate.



Averaged mass spectrum for a DIP temperature around 100°C

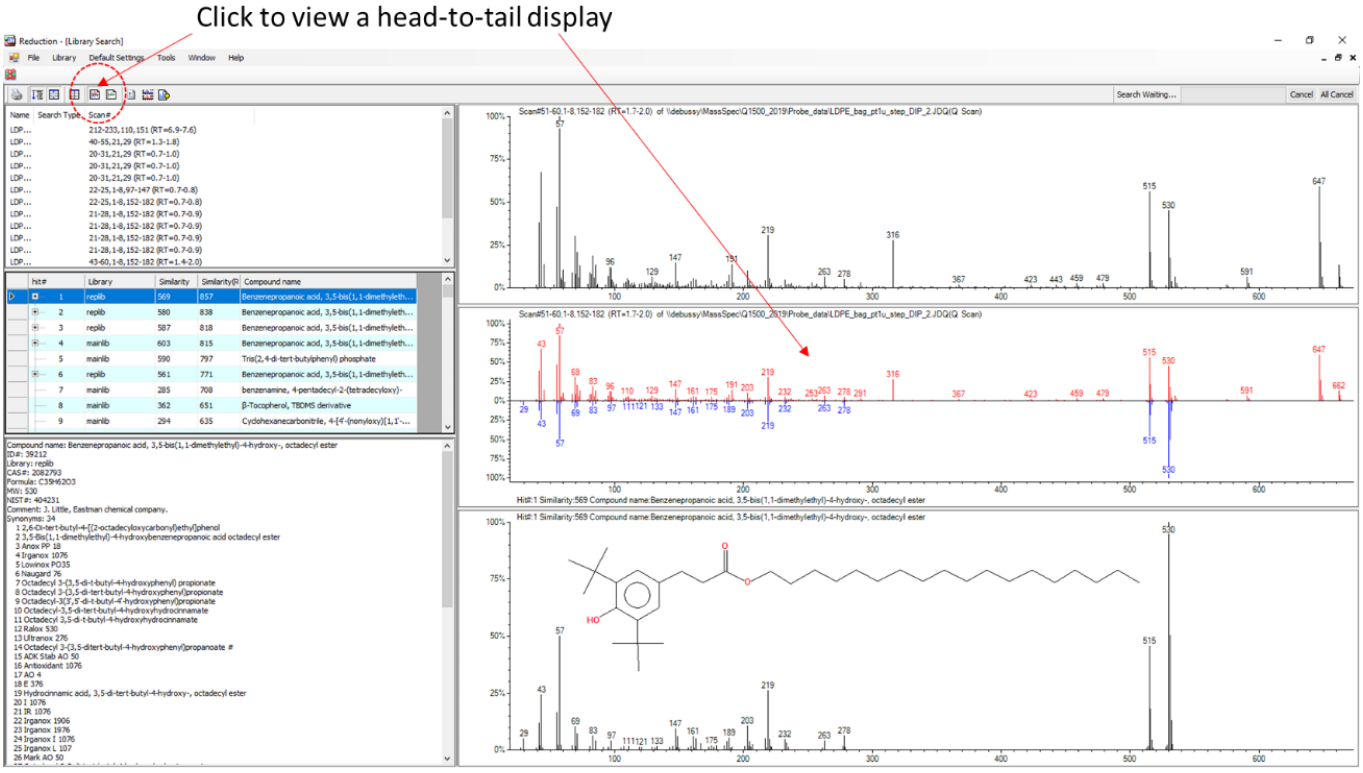




Averaged mass spectrum for DIP temperatures in the range 150-200°C

The mass spectrum for the temperature range 150-200°C shows intense peaks at m/z 515.5, 530.5, 647.5 and 662.5. We can identify candidate compounds by using a reverse search of the NIST Mass Spectral Database.

The top four database matches are for a common polymer additive, benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester. The head-to-tail display shows a good match, but the peaks at *m/z* 647 and 662 are not present in the database spectrum.

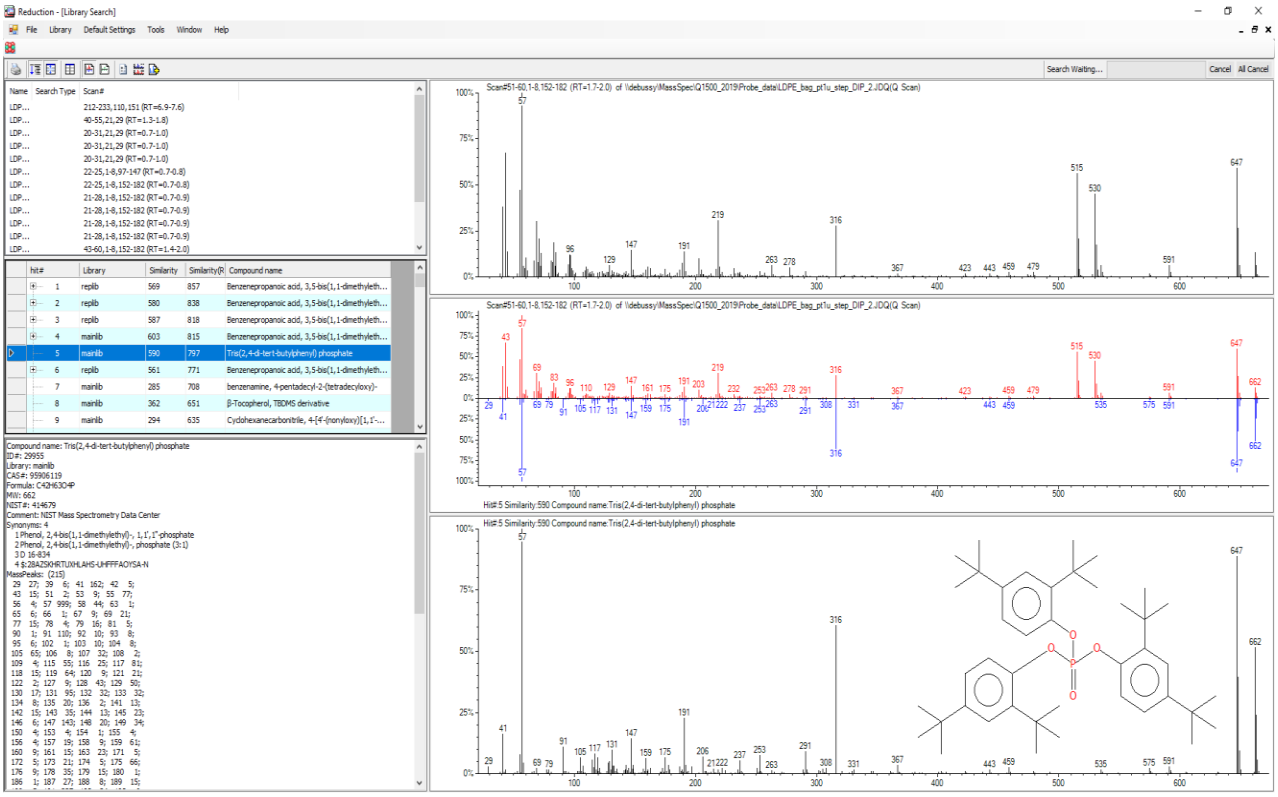


Database match for benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester

hit#	Library	Similarity	Similarity(R	Compound name
1	replib	569	857	Benzenepropanoic acid, 3,5-bis(1,1-dimethyleth...
2	replib	580	838	Benzenepropanoic acid, 3,5-bis(1,1-dimethyleth...
3	replib	587	818	Benzenepropanoic acid, 3,5-bis(1,1-dimethyleth...
4	mainlib	603	815	Benzenepropanoic acid, 3,5-bis(1,1-dimethyleth...
5	mainlib	590	797	Tris(2,4-di-tert-butylphenyl) phosphate
6	replib	561	771	Benzenepropanoic acid, 3,5-bis(1,1-dimethyleth...

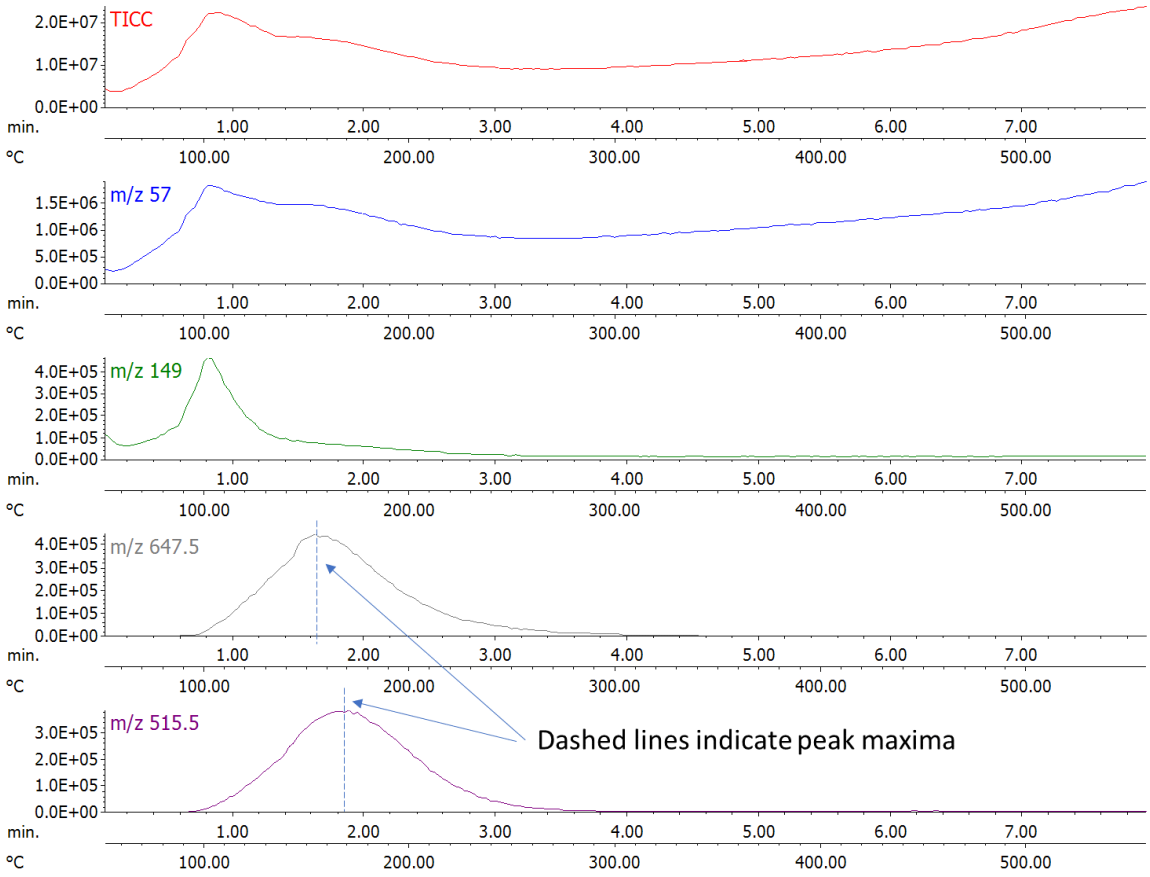
Top database matches

However, the fifth-best match is for another polymer additive: tris(2,-4-di-tert-butyl) phosphate, which *does* contain intense peaks at m/z 647 and 662.



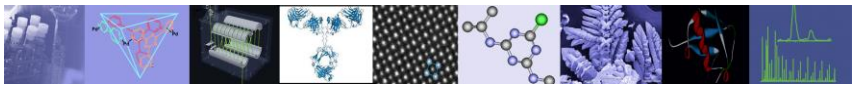
Database match for tris(2,-4-di-tert-butyl) phosphate

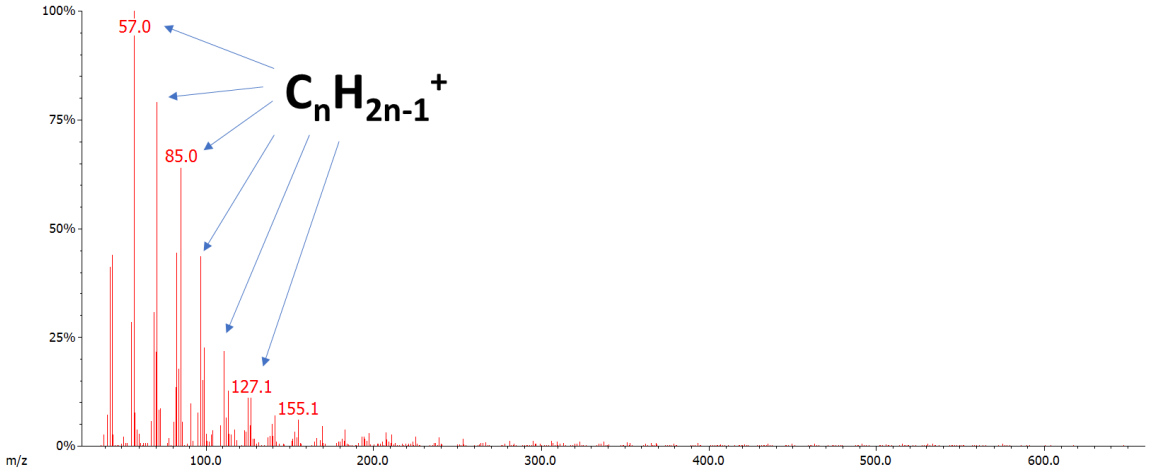
It is apparent that two compounds are desorbing in this temperature range. To verify that these are two different compounds, we can examine the reconstructed ion chronograms for selected *m/z* values.



Total ion current chronogram (TICC) and reconstructed ion chronograms (RICs) for selected m/z's

We can see that *m/z* 647.5 and *m/z* 515.5 have slightly different peak maxima (different temperature dependences), supporting the interpretation that they are coming from two different compounds. Pyrolysis of the polyethylene produces alkyl peaks (*m/z* 57) that rise with time and temperature. As we saw before, the phthalate peak at *m/z* 149 has a sharp maximum at around 100°C. At temperatures above 300°C, we see an increase in hydrocarbon fragment ions at *m/z* 57, 71, 85, 99… resulting from pyrolysis of the polyethylene.





Averaged mass spectrum for DIP temperatures from 300-500°C showing hydrocarbon fragments from polyethylene pyrolysis

Conclusion

The Direct Insertion Probe (DIP) option for the JEOL Q1500GC mass spectrometer provides a fast and easy method for analyzing solid samples that are not well suited for conventional GC/MS analysis. Reconstructed ion chromatograms showing the temperature dependence of peaks at different *m/z* values can provide distinguishing information for mixture components.

References

[1]*T. Pluskal, S. Castillo, A. Villar-Briones, M. Orešič, MZmine 2: Modular framework for processing, visualizing, and analyzing mass spectrometry-based molecular profile data, BMC Bioinformatics 11:395 (2010).* PMID: 20650010

---

11 Dearborn Road, Peabody, MA 01960

Tel: (978) 535-5900 • Fax: (978) 536-2205

ms@jeol.com • www.jeolusa.com