

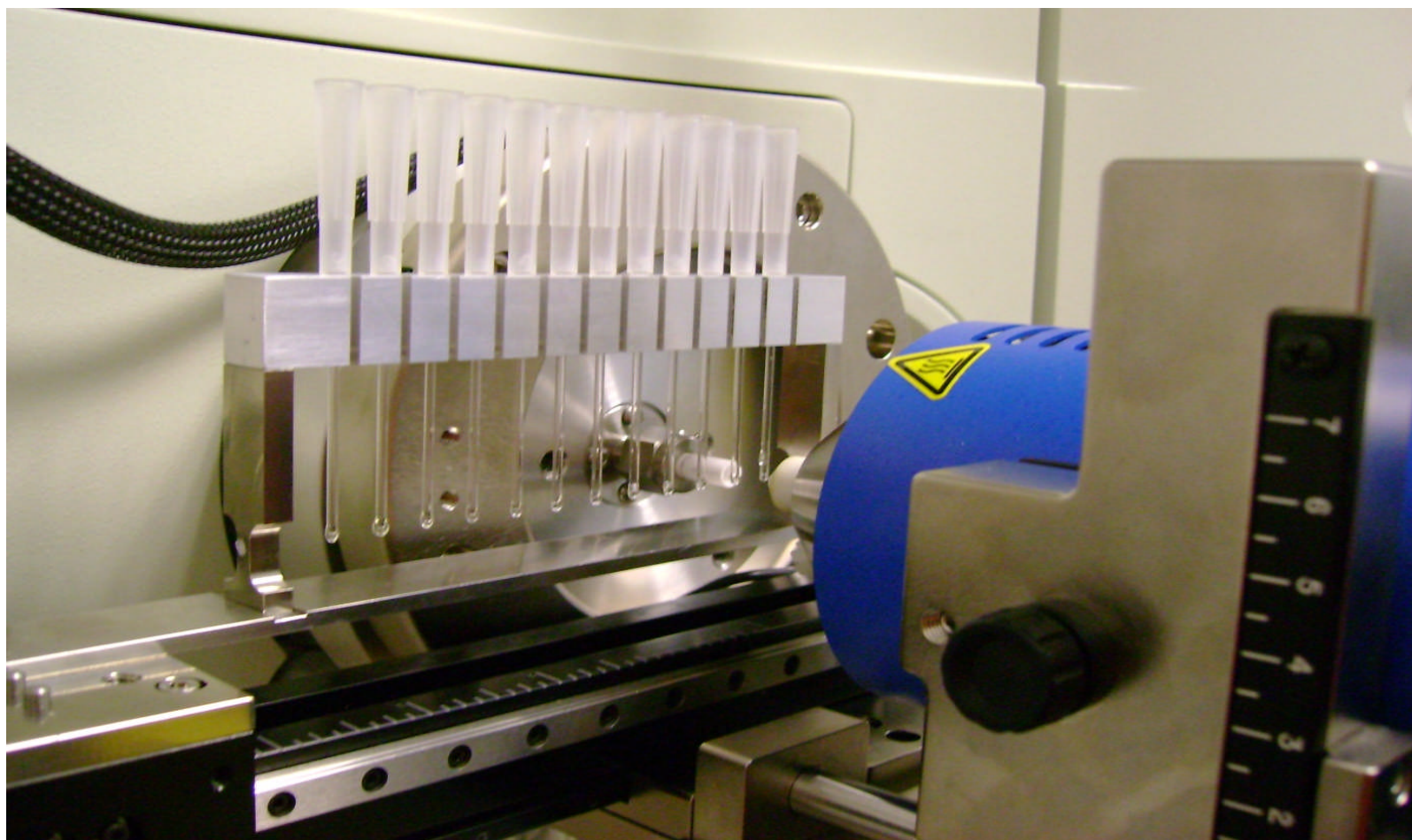
# **Rapid Characterization of Edible Oils for Purity and Composition using Open Air Direct Analysis in Real Time (DART) Mass Spectrometry for Quality Assessment**

B.D. Musselman, E. Crawford, J. Krechmer  
IonSense, Inc., Saugus, MA, USA

## **Abstract**

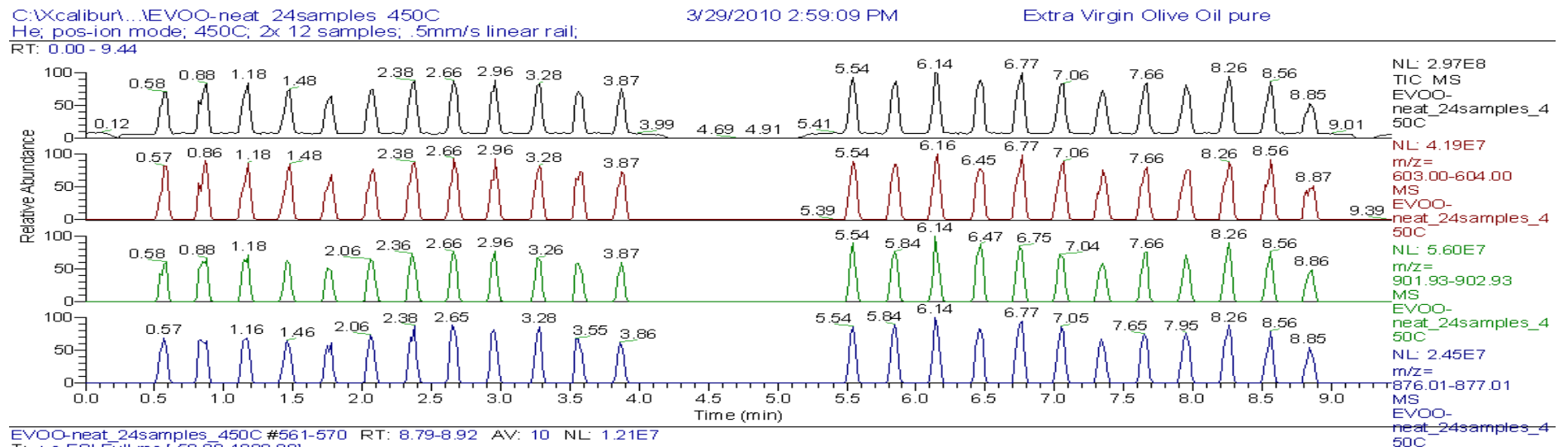
Rapid analysis of edible oils for composition and presence potential adulterants is facilitated by using direct analysis in real time (DART) ionization technique coupled with mass spectrometry. Characterization of the major components of oil including triglyceride, diglyceride and fatty acids without sample preparation is completed in a few seconds per sample. Recently, determination of the distribution of these components in different olive oils has been utilized to differentiate the grade of these oils. We have investigated the use of this technology, operated in a high throughput configuration to permit detection of common adulterants in edible oil including; less expensive oils used for economic adulteration, random contaminants, and non-oil based products that might be mixed with oils in production errors will be described.

The Multi-DIP-it<sup>®</sup> holder moves 12 samples across the ionization stream in under 4 minutes. It allows for extremely consistent and reproducible sampling.

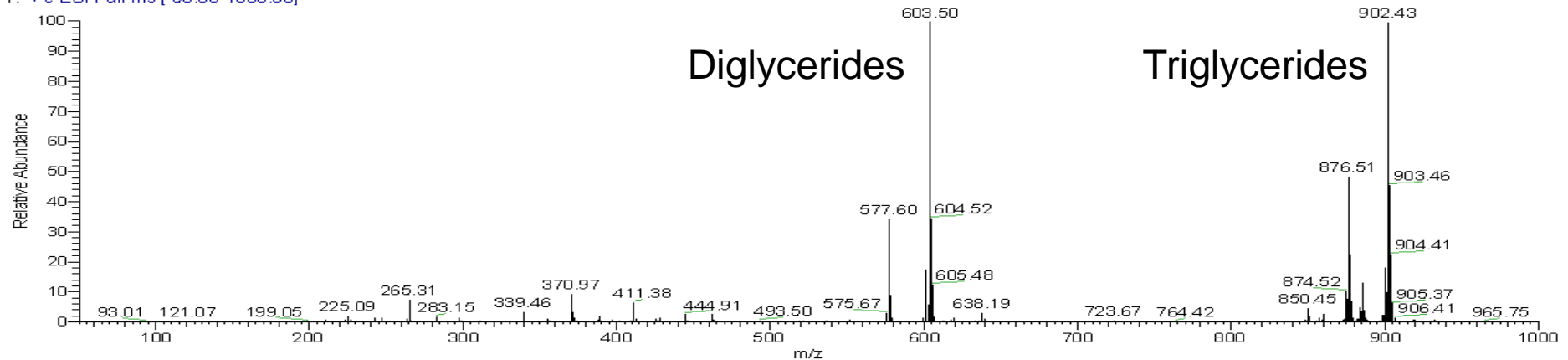


# Mass chromatograms and spectrum obtained from Wild Oats-brand Extra Virgin Olive Oil.

The positive-ion spectrum shows the tri- and di-glycerides with corresponding isotopes. The various extracted-ion chromatograms show the reproducibility of the method over multiple samples.

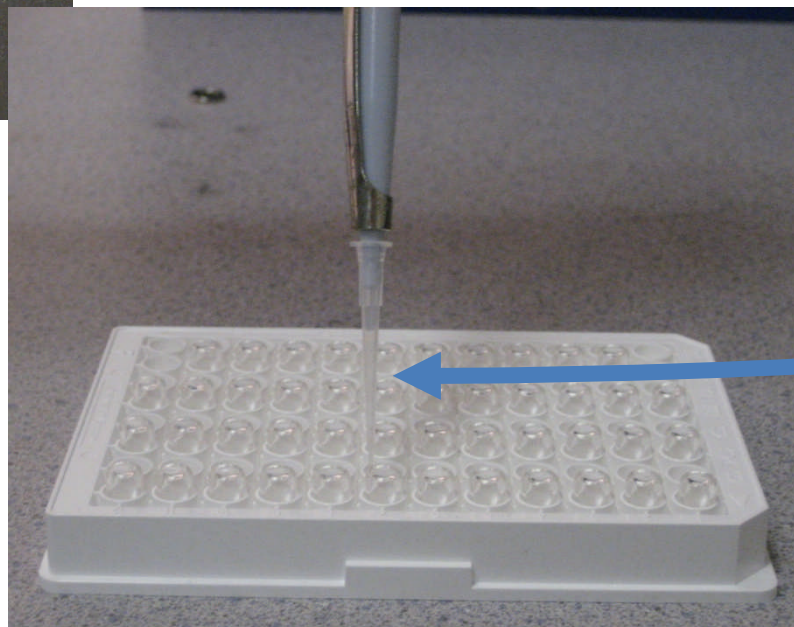
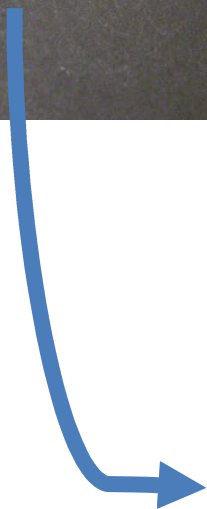
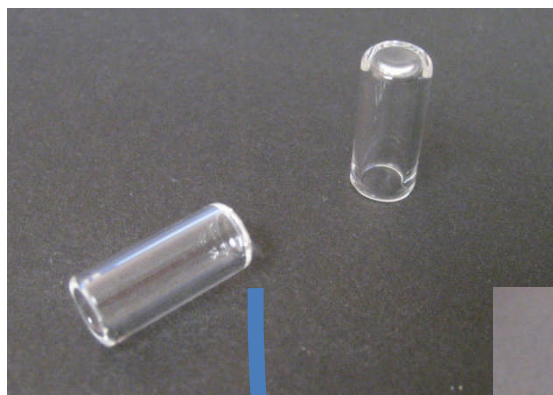


EVOO-neat\_24samples\_450C #561-570 RT: 8.79-8.92 AV: 10 NL: 1.21E7  
 T: +c ESI Full ms [ 50.00-1000.00]



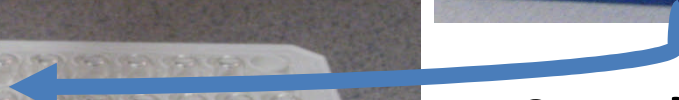
## Desorption Sampler

Glass inserts (SPOT-its™) with small reservoirs on top are inserted into a 96 well-microtiter plate with the closed end up



## Sample Spotting

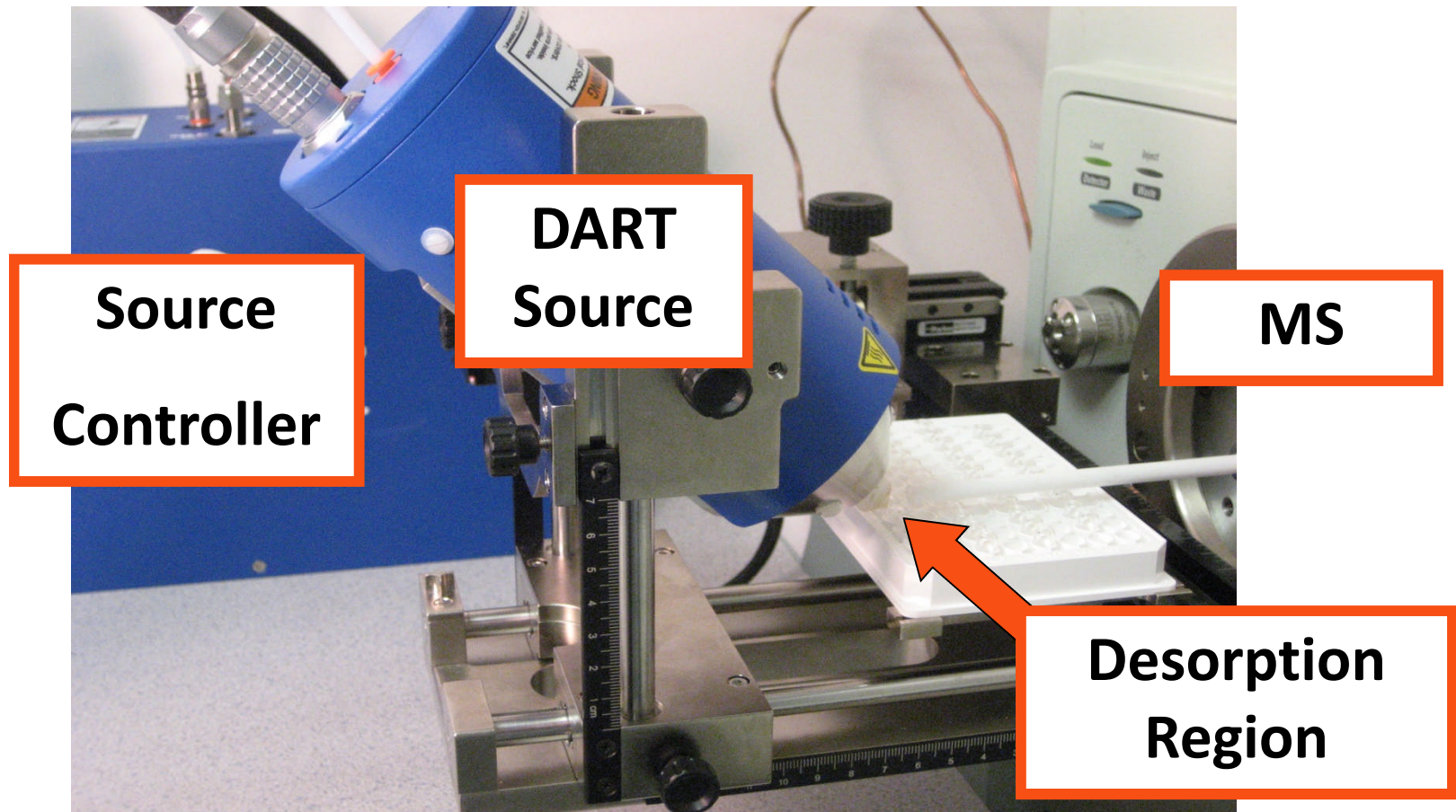
10ul of each oils is pipetted onto the tops of the each insert



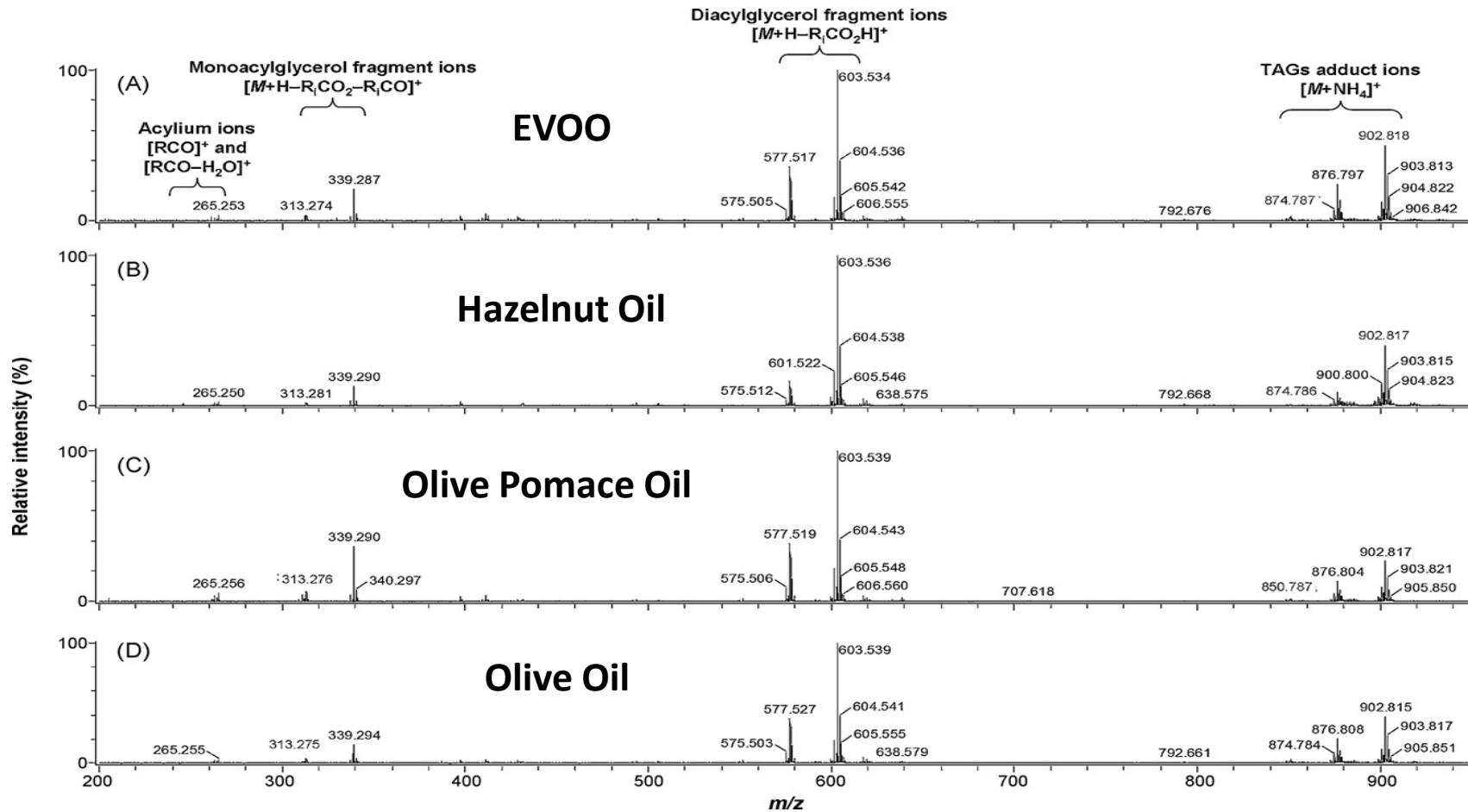
## Sample Array

Sequential positioning of samples allow for rapid MS analysis when the plate is moved to the DART-MS

Sample plate is placed on a X-Y stage with positioning under digital control. Desorption ionization in open air occurs as each individual sample enters the region under the **DART** source gas exit and the **VAPUR** tube leading to the **Ion Trap-MS**.



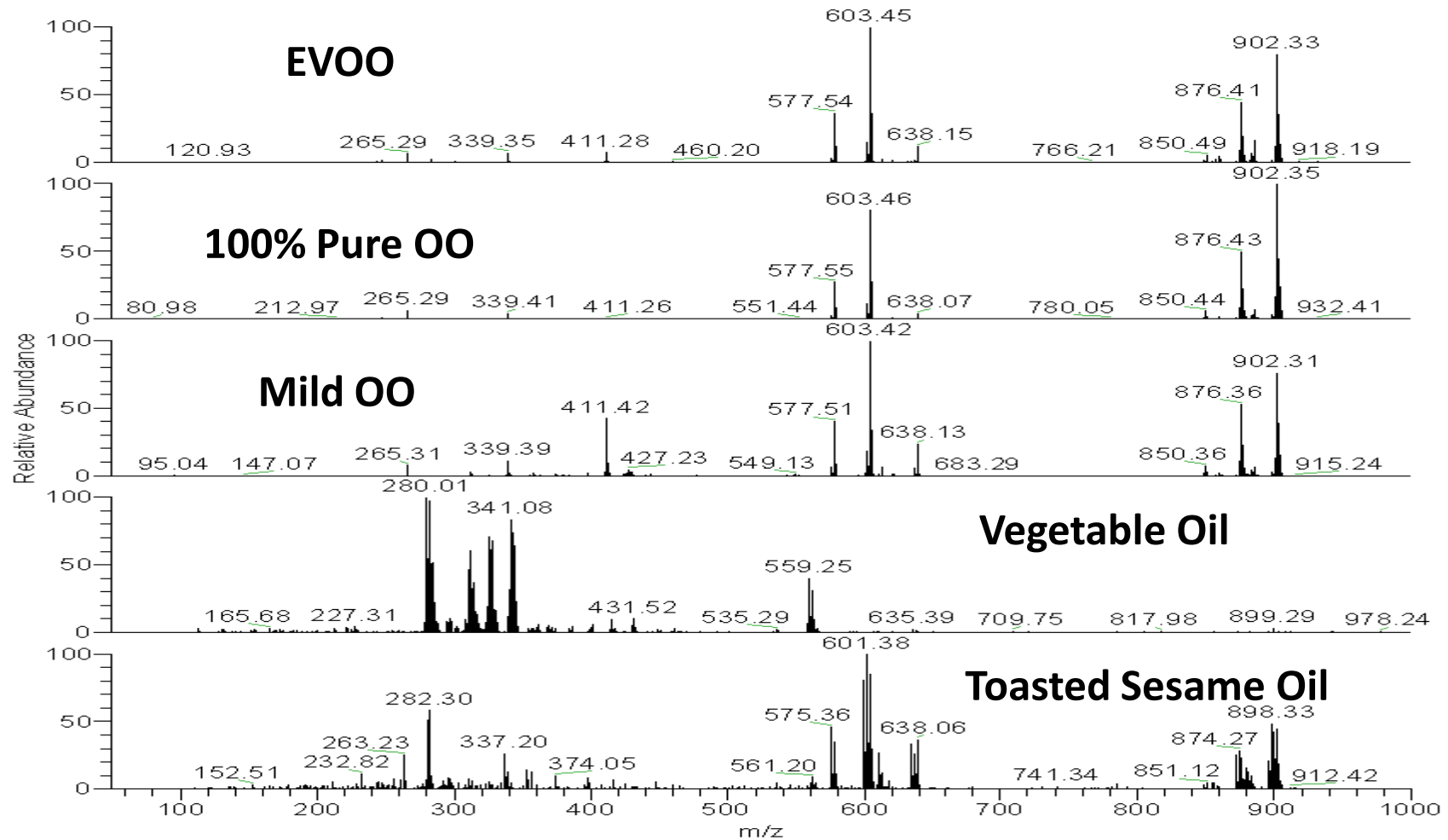
In a recent publication, *Vaclavik et al.* demonstrated the reliable detection of counterfeit olive oils by analyzing samples on a high-resolution DART-AccuTOF instrument (JEOL) and then using linear discriminant analysis to identify adulterated samples.



Pictured above are the spectra of four oils analyzed on an AccuTOF-DART showing the high-resolution triacylglycerols (TAGs) and diacylglycerols produced during the ionization process.

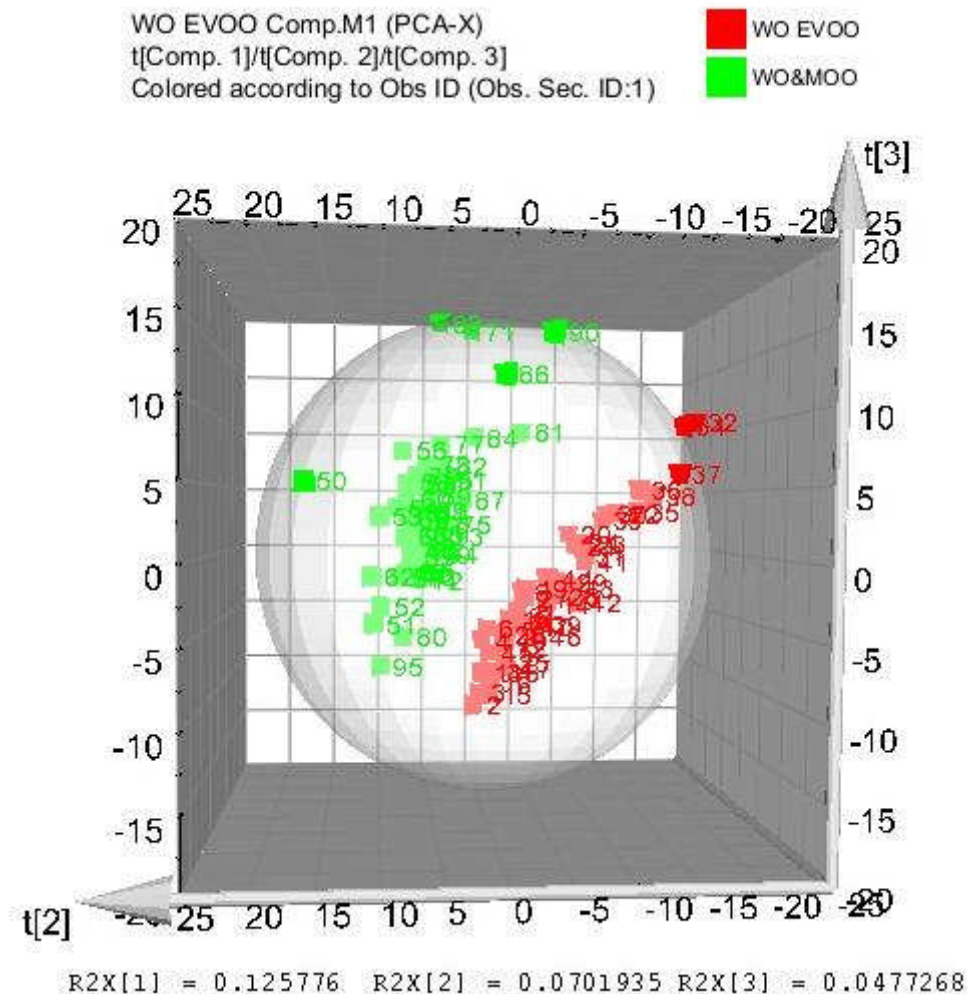
# Positive Ion Spectra of Various Oils

Distinguishing positive-ion spectra from various grades of olive oil is difficult unit however other oils yield quiet different mass spectra.



# Principle Component Analysis

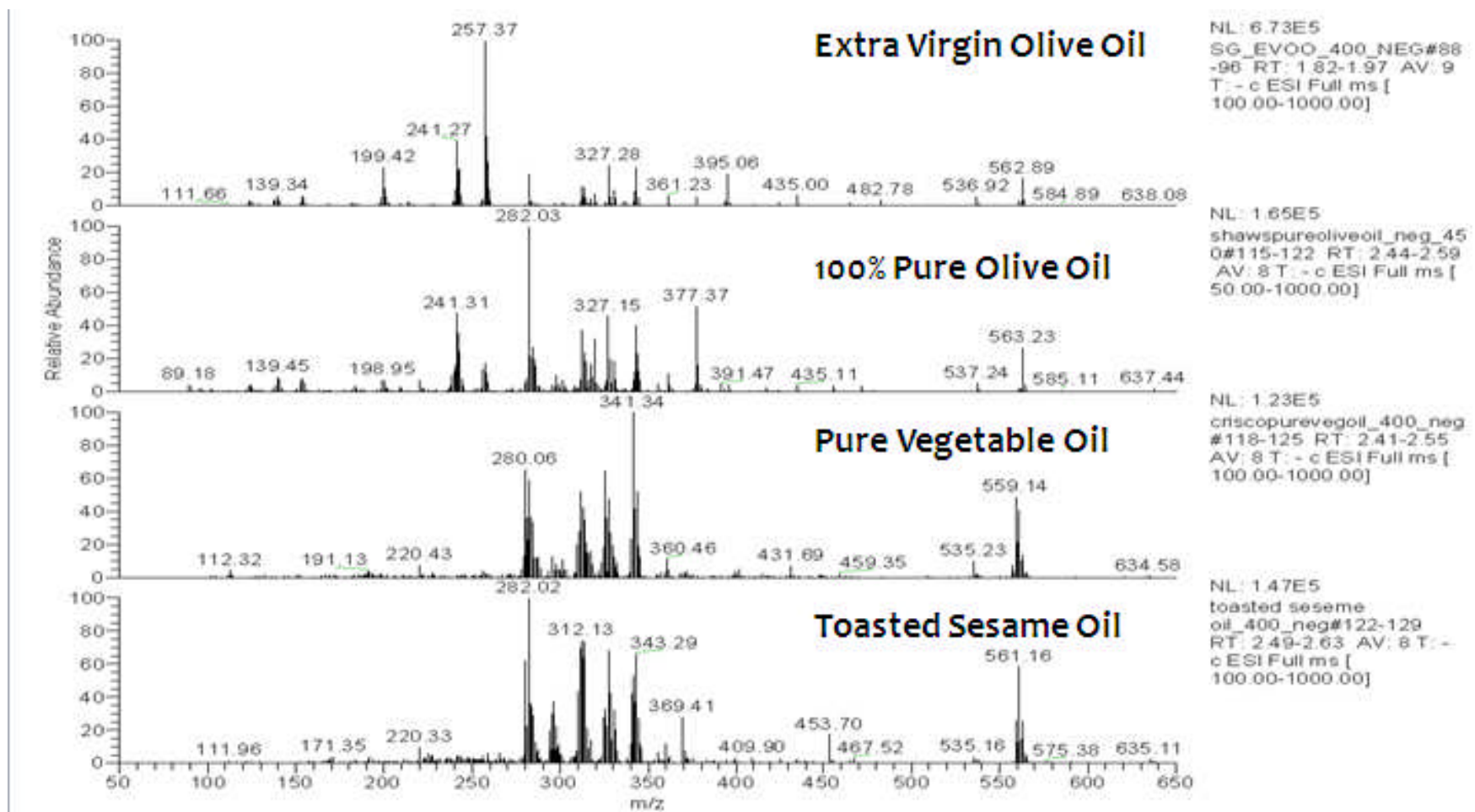
Differentiating the addition of even small percentages of mild olive oil to the olive oil can be detected using PCA statistical analysis



# Negative-ion spectra for five different edible oils

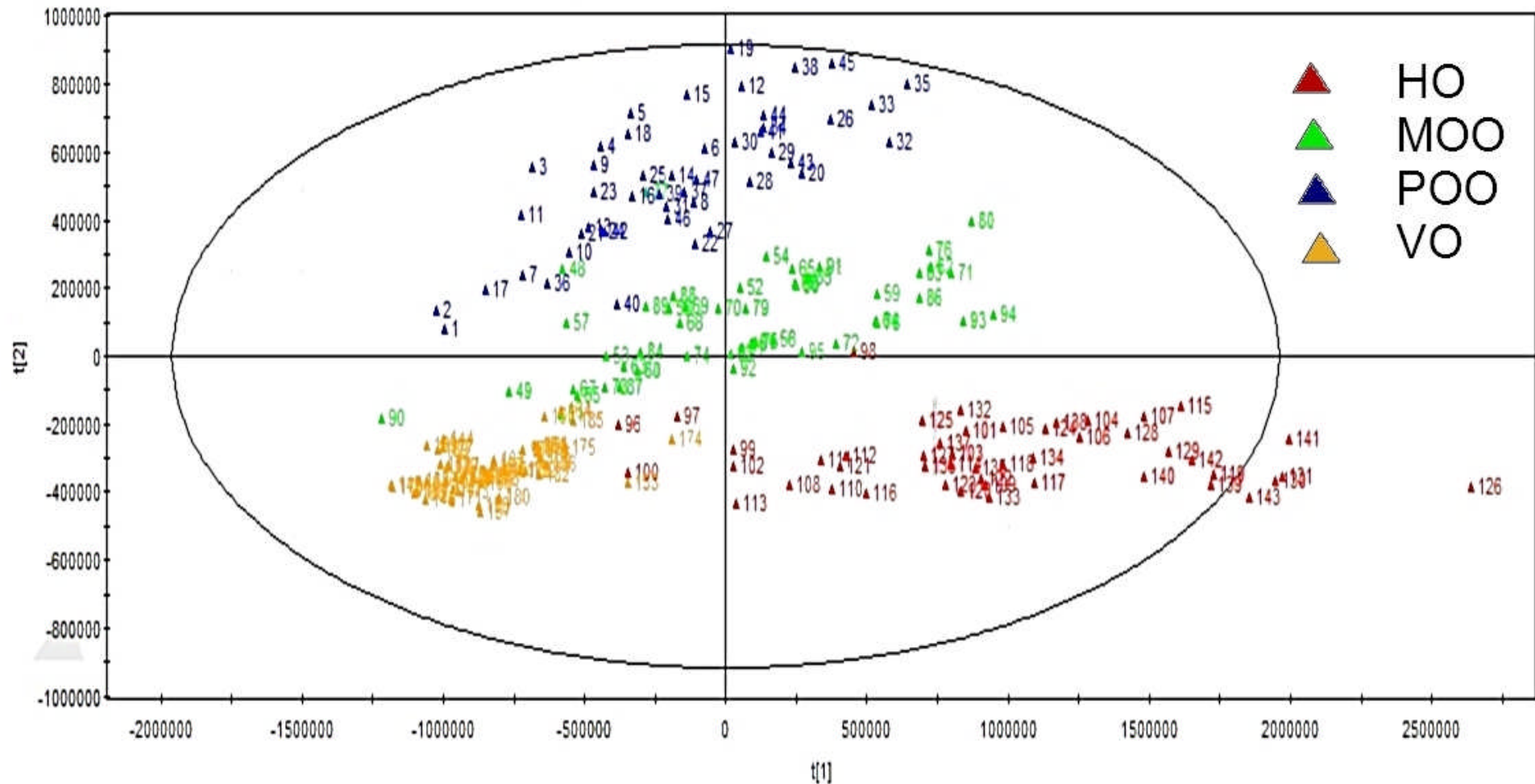
Negative-ion spectra are easily acquired

Major differences in ions and their abundance oils can be used to easily differentiate oil quality and type.



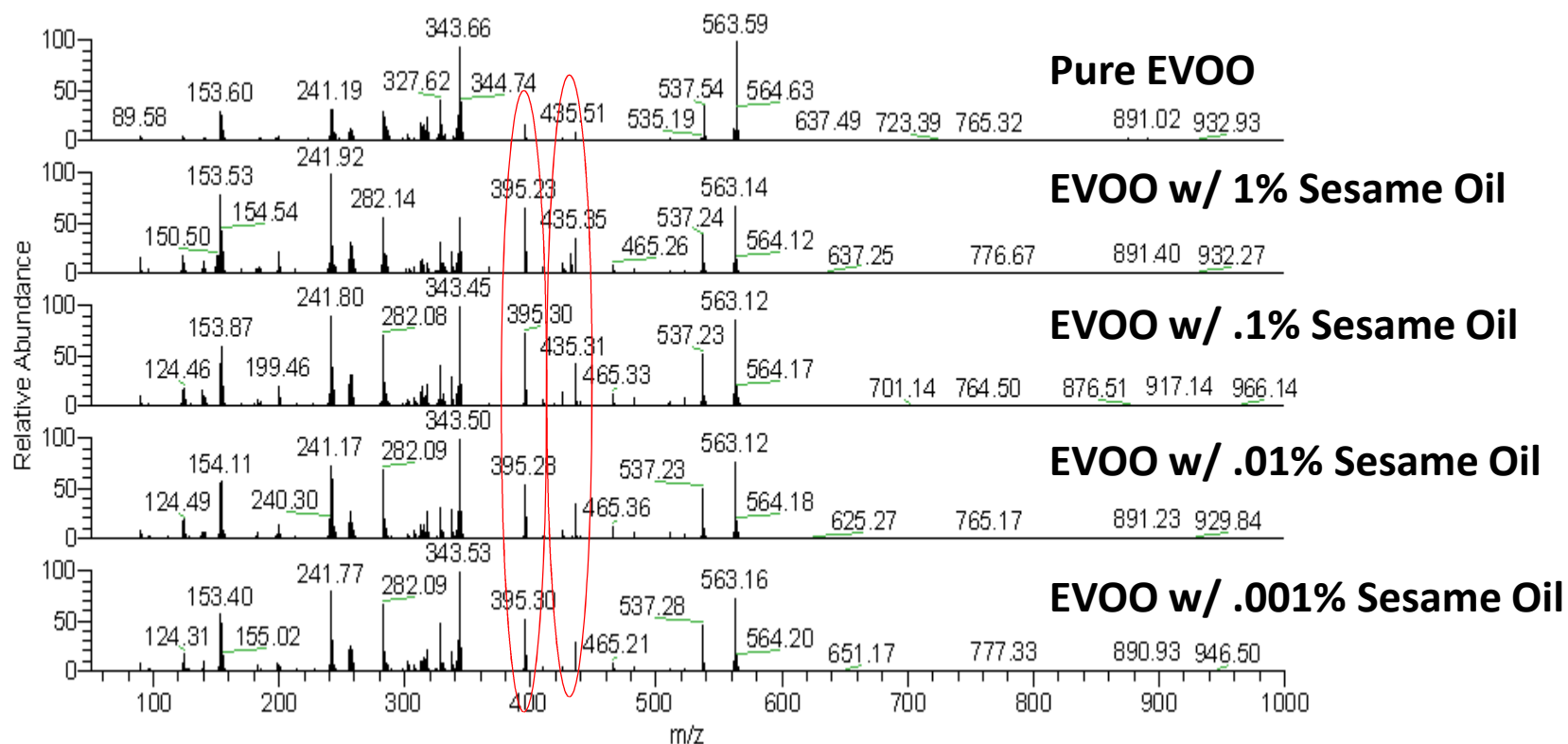
# Principle Component Analysis

PCA of the mass spectra from the different oils provides reasonable differentiation by type

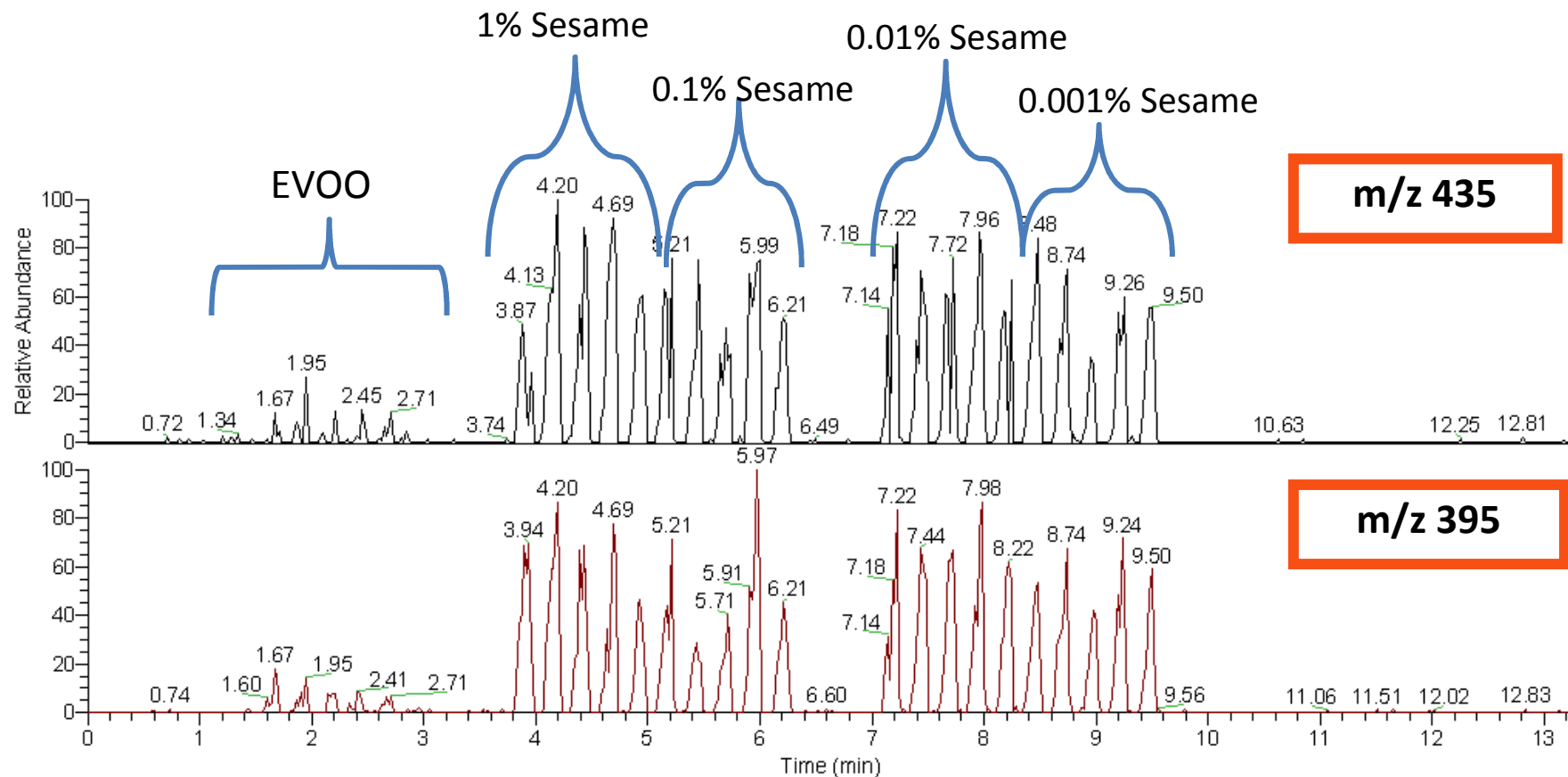


# Detection of Mixed Oils

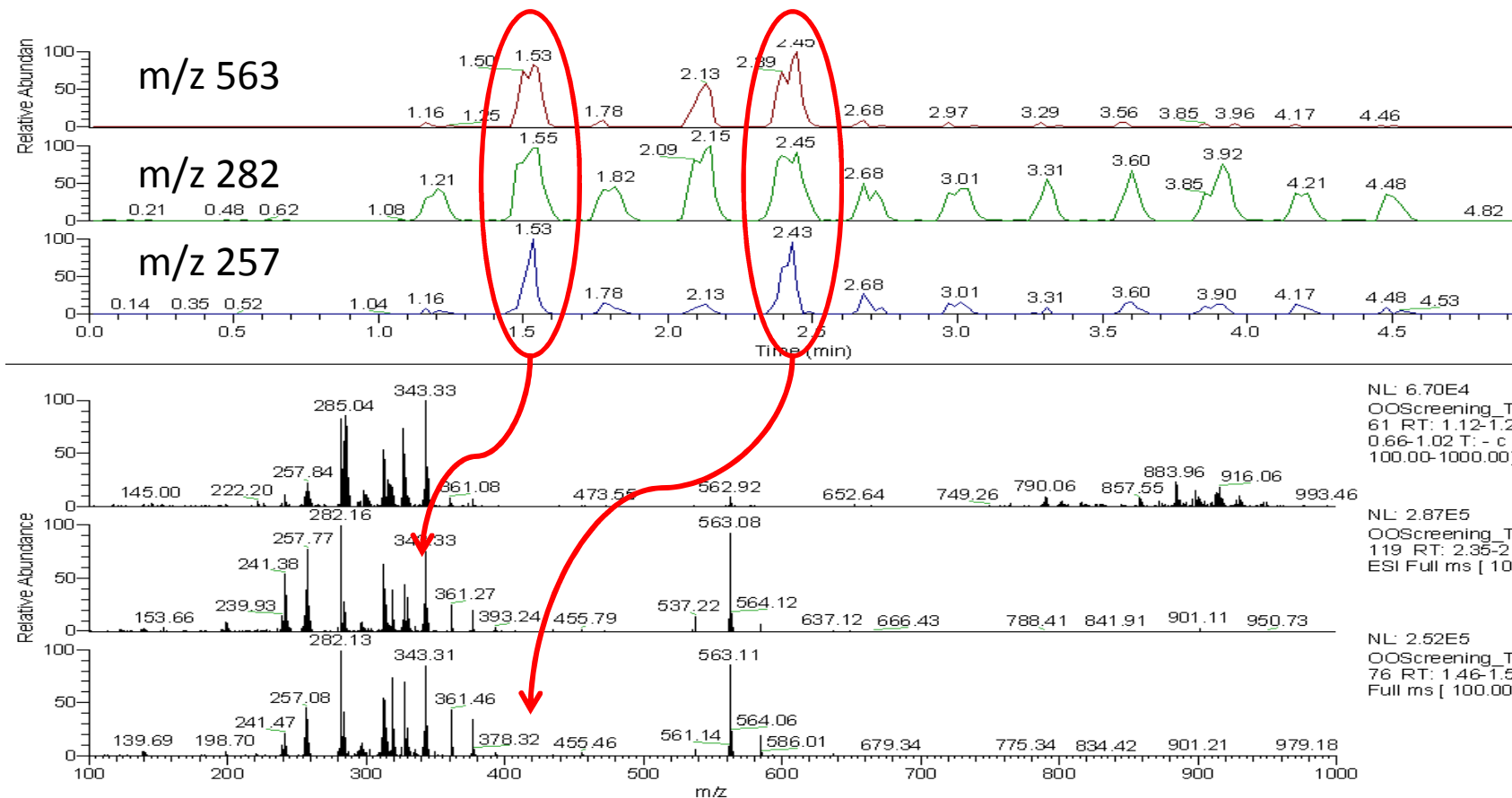
50 ml quantity of olive oil was spiked with 0.5ml of toasted sesame oil and then diluted with olive oil times. The resulting solutions were analyzed using negative-ion DART. The spectra below show that even at low concentrations the 395 and 435 m/z ions which are more abundant in Sesame oil are detected with the Extra Virgin Olive Oil ions.



Pictured below are extracted-ion chromatographs for the circled ions in the spectra on the preceding page. The presence of sesame oil is readily detected at several different concentrations in Extra Virgin Olive Oil (EVOO) by tracking the abundances of two characteristic negative ions. This demonstrates the promise of a rapid screening technique for the detection of edible oil adulterants. The lack of a calibration curve is most likely due to limitations of the ion trap MS.



This slide shows the negative-ion spectrum and extracted ion chromatogram of twelve edible oils samples, of which 10 are Extra Virgin Olive Oil and 2 are Olive Oil. The relative abundance of  $m/z$  563 and 257. In the extracted ion chromatogram the two olive oil peaks are clearly identified.



# Conclusions

- Rapid production of mass spectra containing intact protonated TAG's is feasible with DART
- Detection of mixtures of different oils in seconds facilitates more active screening of raw materials for possible adulteration
- PCA provides a tool for automated inspection of oil quality and authenticity
- New Open Air Technology capable of reducing thermal degradation during ionization is in development

# References

- *L. Vaclavik et al. / Analytica Chimica Acta 645 (2009) 56–63*
- Cody, R.B.; Laramée, J.A.; Durst, H.D. *Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions. Anal. Chem.*, 2005, **77**(8), 2297-2302.