

# DIFFERENTIATING COMMERCIAL LUBRICANT OILS USING ION-MOBILITY ENABLED MASS SPECTROMETRY

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## INTRODUCTION

Lubricant oils are used in a vast array of industrial applications, from domestic car engines, to oil well drilling rigs, to specialist metalworking machinery; in fact, lubricant oils may be found in any situation where surfaces contact one another and friction might become a problem.<sup>1,2</sup> Due to their wide range of uses, many different formulations of lubricant oils are manufactured.



Figure 1. The lubricant oil samples.

A variety of approaches can be used to understand the quality and condition of a lubricant oil.<sup>3-6</sup> Here we outline a simple and efficient workflow that uses high-resolution mass spectrometry and statistical analysis of the acquired data, to understand the differences between five automotive lubricant oils at a molecular level. This approach could be particularly useful in comparing two similar products, identifying the differences between poorly performing and correctly performing oils, or deformulating competitors' products.



Figure 2. The SYNAPT G2-Si HDMS instrument.

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## METHOD

### Sample preparation:

Five commercial automotive lubricant oils (Figure 1) were purchased off the shelf. All oils were classified as 5W/30 synthetic oils. The oils were diluted to a concentration of 100 µg/mL in 90:10 toluene:methanol + 0.1 % formic acid.

### Sample introduction:

The samples were introduced, by loop injection (0.5 µL), into a high-resolution, ion-mobility enabled mass spectrometer.

### SYNAPT G2-Si HDMS conditions:

An ESI source was installed on a SYNAPT G2-Si HDMS instrument (Waters Corporation) (Figure 2). The samples were analysed using ESI+ in HDMS<sup>E</sup> mode.

Ion mobility-HDMS<sup>E</sup> conditions were optimized as follows:

- Capillary voltage: 1 kV
- Cone voltage: 30 V
- Source temperature: 150 °C
- Desolvation temperature: 250 °C
- Desolvation gas flow: 1000 L/Hr
- Cone gas flow: 0 L/Hr
- HDMS<sup>E</sup> collision energy: 20–75 eV
- IMS Wave velocity: 1000–300 m/s
- IMS Wave height: 40 V
- IMS cell pressure: 3.2 mbar
- Mass Resolution: 40K
- Mass range: 50–1200 *m/z*

### Data Acquisition and Processing:

Data were acquired using MassLynx v4.2, and processed using UNIFI v1.9 with EZInfo v3.0.

## RESULTS & DISCUSSION

HDMS<sup>E</sup> data acquisition followed by UNIFI data processing, with Multi Variate Analysis (MVA), was successfully used to differentiate five commercially available lubricant oils.

A Principle Component Analysis (PCA) score plot (Figure 3) showed that the five lubricant oils were able to be separated using this approach, and the associated loading plot (Figure 4) highlighted marker ions responsible for the differences. Trajectories within the loading plot indicate markers related to each sample, with those markers further from the origin of the plot being more significant.

Markers discovered within each trajectory were targeted using the UNIFI software to confirm their prevalence in a specific lubricant oil. Examples of the responses for three markers across all samples are displayed in summary plots (Figure 5). Ion mobility enabled the elucidation of markers through the generation of clean spectra with associated fragment ions, in the absence of chromatographic separation (Figure 6). The marker *m/z* 338.28 was proposed as Antioxidant L 57 (Figure 7).

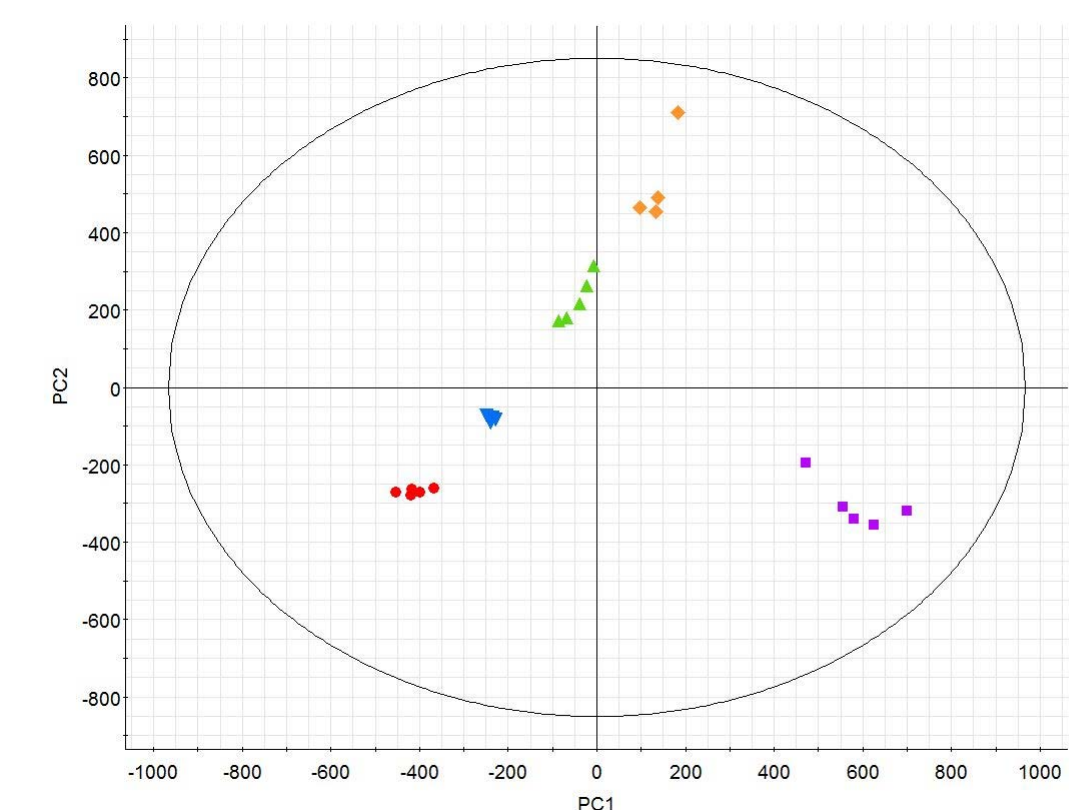


Figure 3. PCA score plot showing that the five lubricant oils are clearly separated.

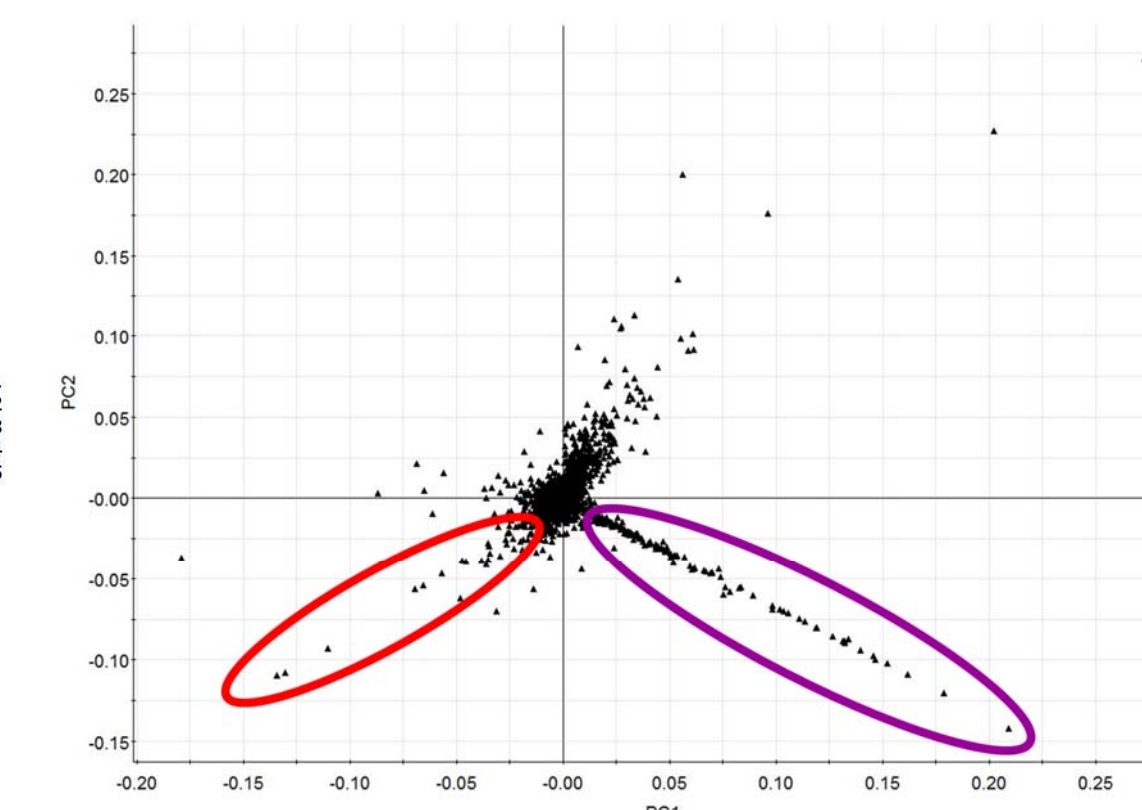


Figure 4. PCA loading plot showing markers that are more significant to lubricant 2 (purple ellipse) and lubricant 3 (red ellipse).

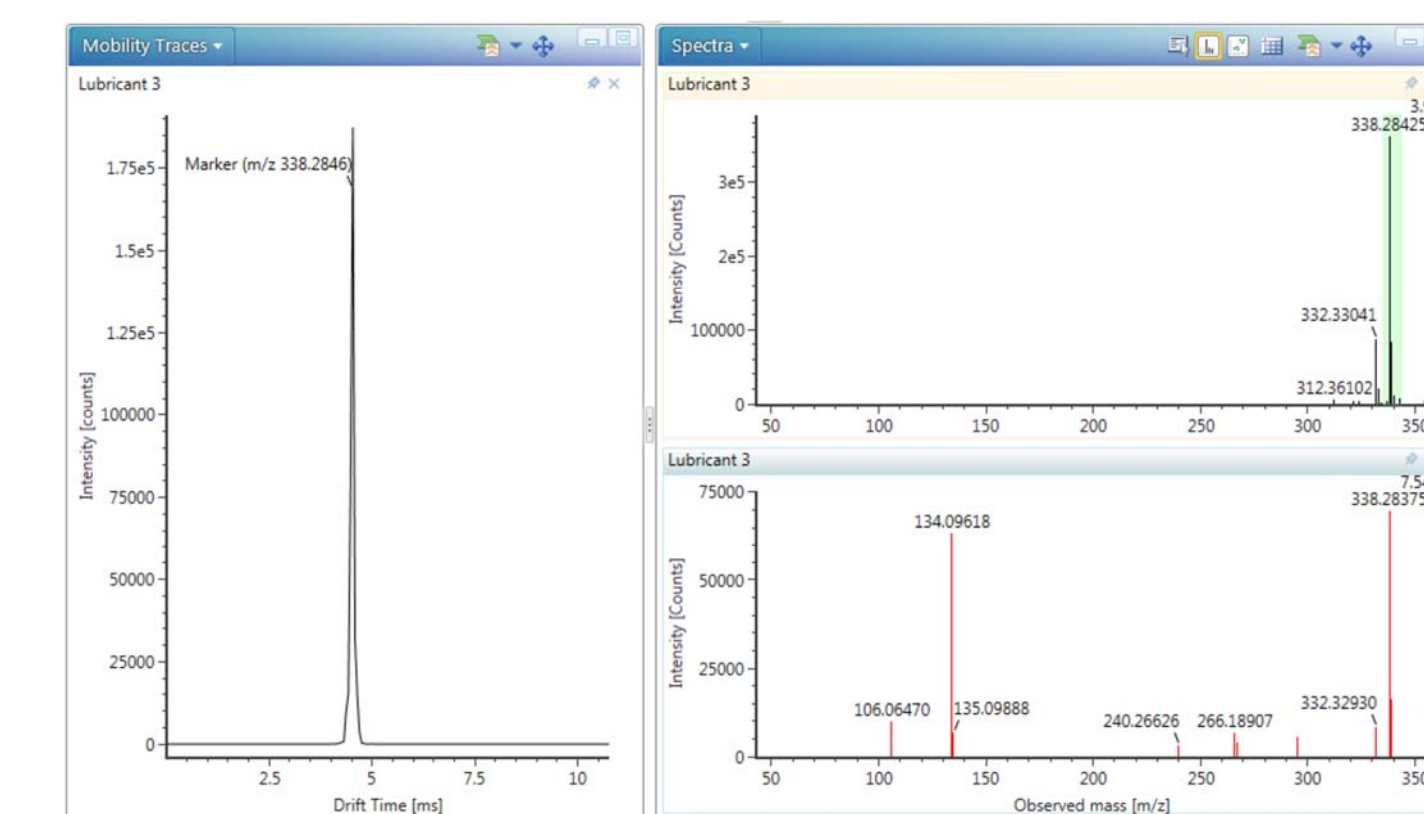


Figure 6. Extracted ion mobiligram (left) with related low energy precursor ion spectrum (upper right) and high energy fragment ion spectrum (lower right).

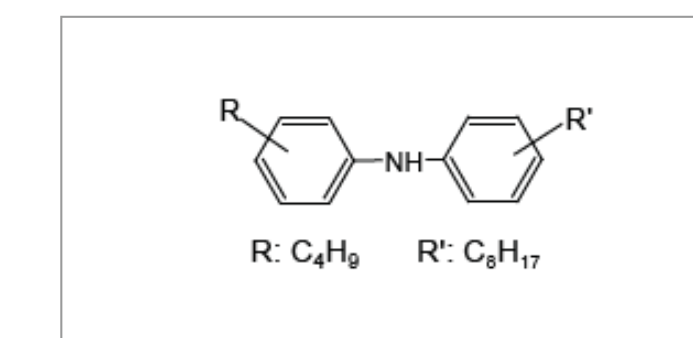


Figure 7. Antioxidant L 57, identified as possible structure for marker *m/z* 338.28.

### Acknowledgments

With thanks to Waters colleague Mike McCullagh for ongoing technical support and useful discussions.

## CONCLUSION

- Acquire HDMS<sup>E</sup> data
- Process HDMS<sup>E</sup> data
- Determine markers using MVA
- Elucidate selected markers
- Confirm selected markers using compound standards

- Five commercial lubricant oils were successfully differentiated using the proposed workflow shown above
- UNIFI software facilitated the discovery of key markers that caused the differences between the lubricant oils
- Elucidation of the markers enabled tentative identification of the compounds in the lubricant oils
- Further work will involve the confirmation of tentatively identified compounds through the purchase and analysis of standards

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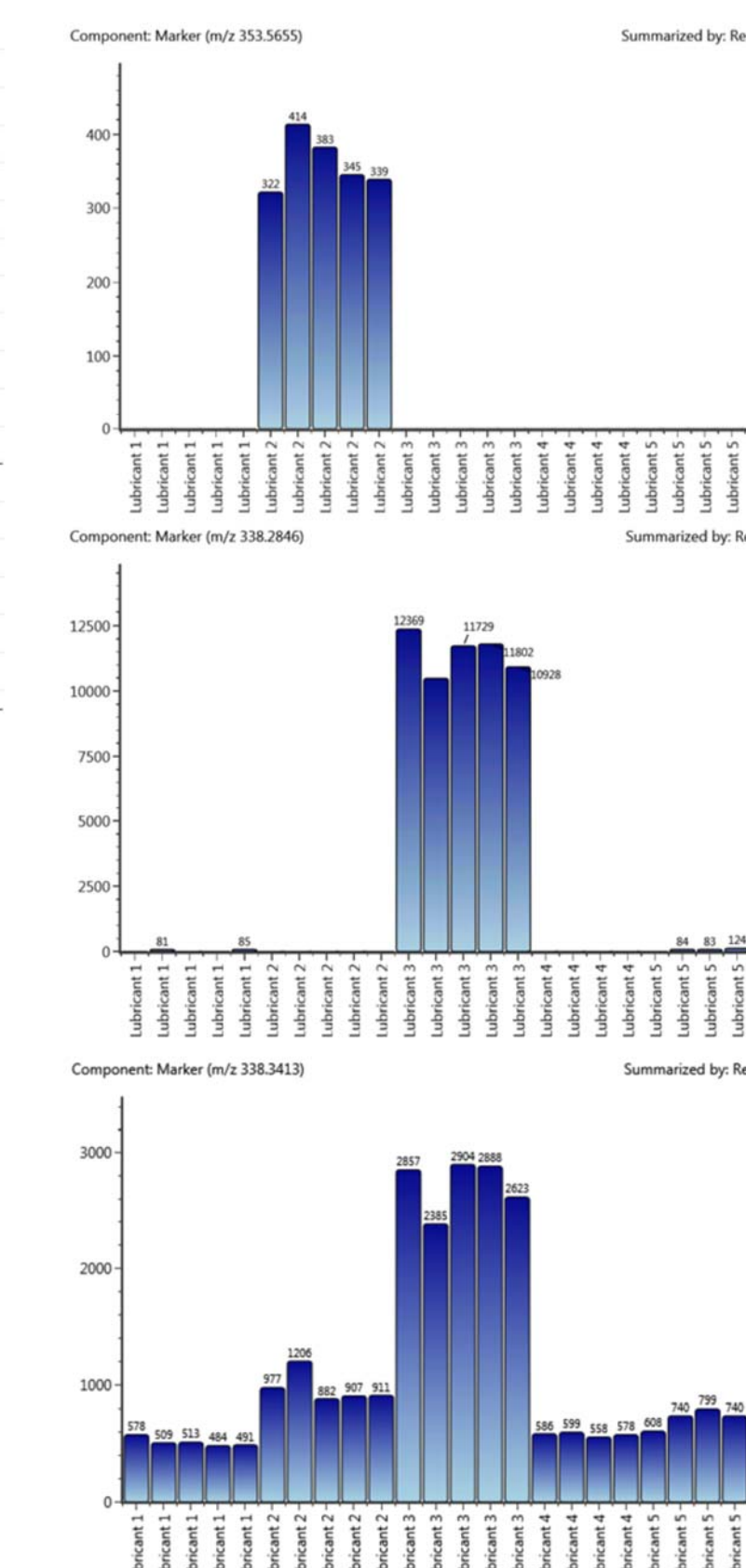


Figure 5. Summary plots showing examples of key markers for lubricant oil 2 (upper plot) and lubricant oil 3 (middle and lower plots).