

THE APPLICATION OF ION-MOBILITY ENABLED MASS SPECTROMETRY TO DISTINGUISH BETWEEN COMMERCIAL LUBRICANT OILS

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INTRODUCTION

Lubricant oils are used in many commercial settings, from the automotive and aerospace industries, to oil well drilling rigs, to specialist metalworking machinery; in fact, lubricant oils may be present in any application where surfaces might contact one another and friction become a problem.^{1,2} Many different formulations of lubricant oils are manufactured to address their wide range of uses.



Figure 1. The lubricant oil samples.

High resolution mass spectrometry enables the accurate mass measurement of ions from which molecular information may be derived.³ The specificity of the approach is further enhanced by ion-mobility, which provides information related to the size, shape and charge of the ions.^{4,5}

A simple workflow, combining ion-mobility with high resolution mass spectrometry followed by statistical analysis of the acquired data, is presented. This technique is used to discover differences between five automotive lubricant oils at the molecular level. This approach could be used to compare similar products, understand the differences between poorly performing and correctly performing oils, or to reformulate competitors' products.

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. Five replicates of each sample were acquired in a random order.

SYNAPT XS HDMS:

An ESI source was installed on a SYNAPT XS HDMS instrument (Waters Corp., UK) (Figure 2). The samples were analysed using ESI+ in HDMS^E mode.



Figure 2. The SYNAPT XS HDMS instrument.

Data Acquisition and Processing:

Data were acquired using MassLynx v4.2 (Waters Corp., UK), imported into and processed with UNIFI v1.9 (Waters Corp., UK). Statistical processing was carried out with the multivariate analysis software EZInfo v3.0 (Umetics, Sweden).

RESULTS & DISCUSSION

HDMS^E 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). In the absence of chromatographic separation, ion mobility enabled the generation of clean spectra that contain precursor ions and their associated fragments (Figure 6), which aided the elucidation of markers. The marker *m/z* 413.3023 was proposed to have the molecular formula C₂₅H₄₂O₃, with a sodium adduct, which was tentatively suggested to be the anti-oxidant octyl-3,5-di-tert-butyl-4-hydroxy-hydrocinnamate (Figure 7).

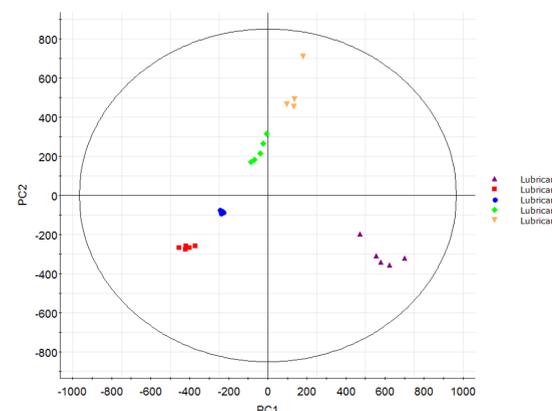


Figure 3. PCA score plot showing that the five lubricant oils are clearly separated.

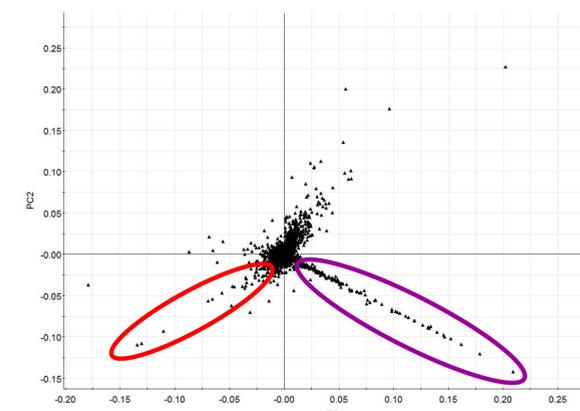


Figure 4. PCA loading plot showing markers that are more significant to lubricant 2 (purple ellipse) and lubricant 3 (red ellipse).

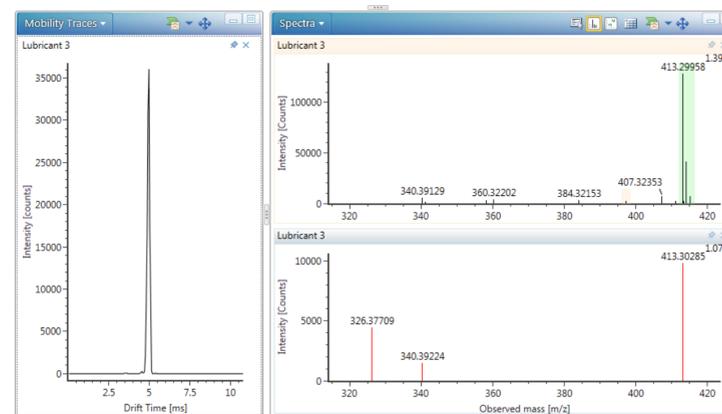


Figure 6. Extracted ion mobility trace (left) with related low energy precursor ion spectrum (upper right) and high energy fragment ion spectrum (lower right).

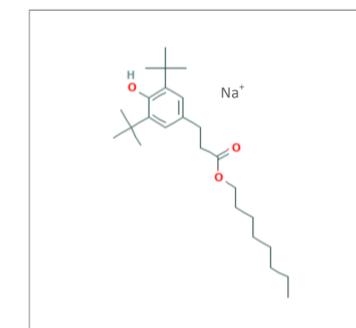


Figure 7. The sodium adduct of octyl-3,5-di-tert-butyl-4-hydroxy-hydrocinnamate (molecular mass 390.3134) is tentatively assigned to the marker *m/z* 413.3023.

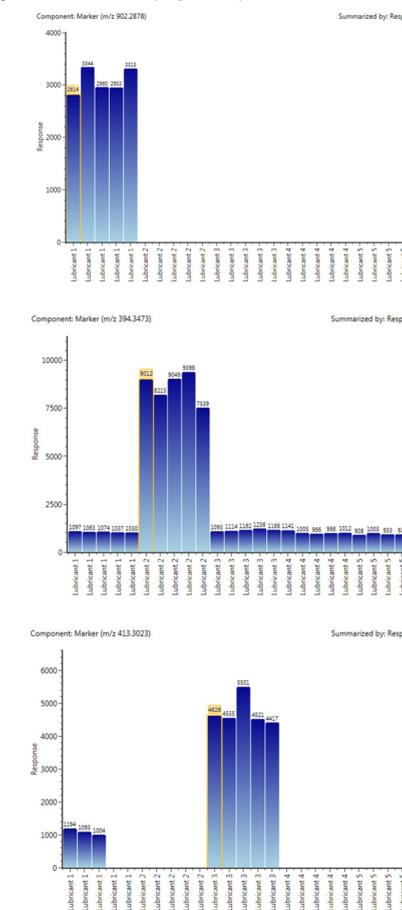


Figure 5. Summary plots showing examples of key markers for lubricant oils 1, 2 and 3.

CONCLUSION

- Acquire HDMS^E data
- Process HDMS^E 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 and EZInfo 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.

References

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