Characterization of semi-synthetic motor oil using FT-ICR

Sung Hwan Yoon, David R. Goodlett, and David P. A. Kilgour

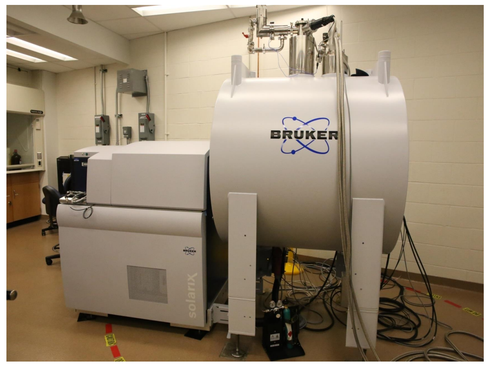
University of Maryland – Baltimore, Pharmaceutical Science, Baltimore BD

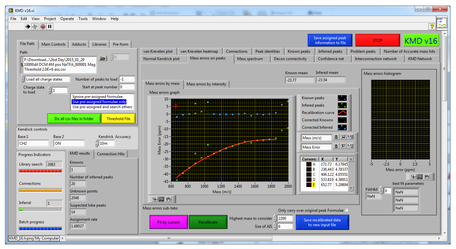
Goodlett Laboratory

Introduction

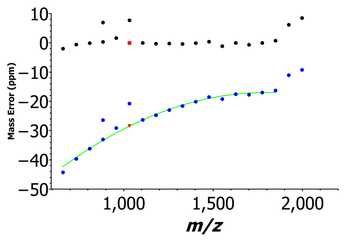
Automotive lubricant oils are either mineral oil, fully synthetic oil or a mixture of both classes. Synthetic motor oils commonly use polyalkylene glycols, polyesters, or polyalphaolefins. Additives are used to protect the oil and adapt the performance. During use, the motor oil and the additives are degraded and contaminated with burn products and degradation products. Traditional methods for the characterization of fresh and used oil have been based on FT-IR, NMR, or GC-MS techniques. Here we have used absorption mode FT-ICR MS to provide an alternative or complementary method for the analysis of motor oil. A semi-synthetic 5W20 oil was analyzed and the same type motor oil was collected from a domestic automobile after 200 and 3,500 miles normal use.

For laser desorption ionization (LDI), a 1μL of the oil solution was dissolved into 100μL of methanol and dichloromethane (2:1 v/v). A 1μL of sodium trifluoroacetate (100ug/mL in MeOH:H2O 1:1 v/v) was spiked in the oil solution. For ESI, a 1μL sample was dissolved into a mixture of 10 mL of methanol and dichloromethane (2:1 v/v). A 10μL of sodium trifluoroacetate (100ug/mL in MeOH:H2O 1:1 v/v) was spiked in the oil solution and served as an internal calibrant. Spectra were recorded on a Bruker 12T Solarix XR and the data was converted to absorption mode using Autophaser. Molecular formulae were assigned using SmartFormula 3D (Bruker Daltonics) and nD KMD. End groups on the polymer components in synthetic lubricant were assigned using the methods of va Rooij et al.



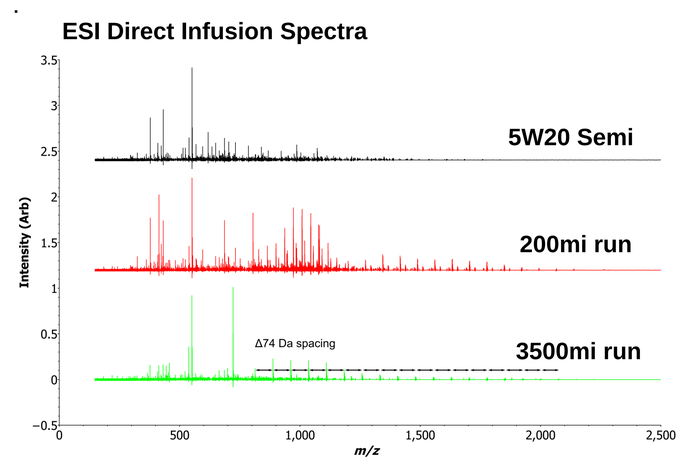


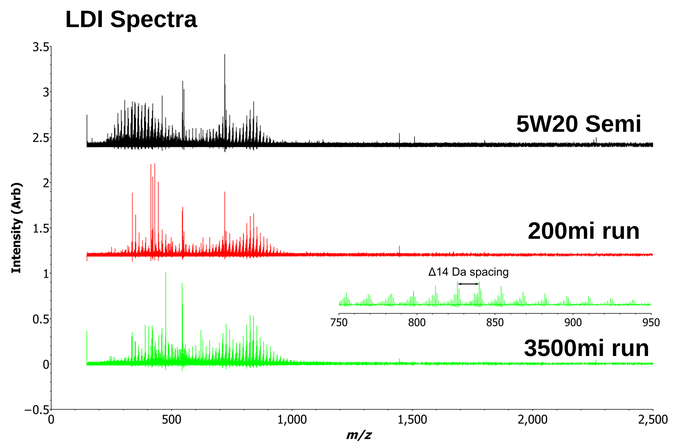
nD KMD user interface

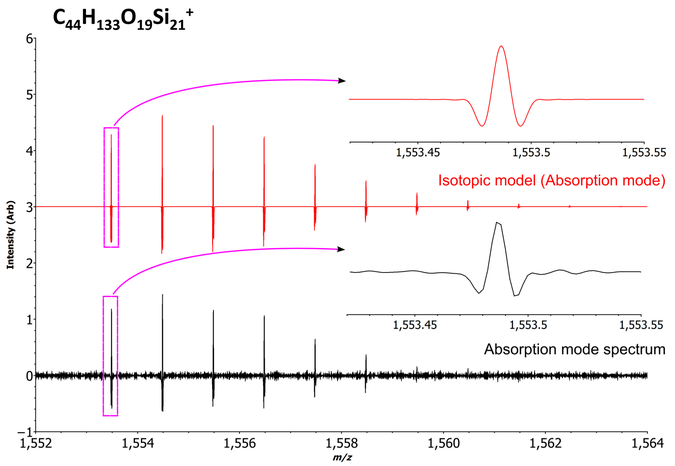


Mass recalibration graph from nD KMD showing PDMS series before (blue)and after calibration (black). nD KMD ignores anomalies from calibration curve data automatically. Red points are the two originally identified peaks, the other points were automatically inferred.

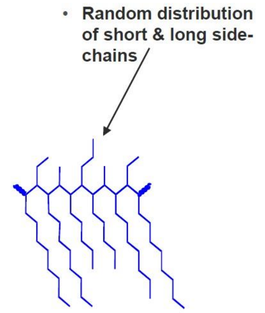
Direct Infusion & Laser Desorption Ionization







The trimethylsilyl PDMS series could be easily identified using the isotopic distribution of the homologous series members. In order to plot isotopic distributions in the absorption mode we use a modified version of the Mercury algorithm (Kilgour et al.).



Conventional PAO

PAO figure from ExxonMobil website

Conclusions

Both LDI and ESI successfully generated spectra from the test oil samples. Because semi-synthetic oil is a mixture of mineral oils and synthetic oils, many peaks are observed for each sample but high resolving power of ICR mass spectrometer, especially in absorption mode, enables assignment of the molecular formulae to a large proportion of the peaks. In the ESI spectrum, polydimethylsiloxane (PDMS) was shown after 3,500 mi run. It is common lubricant material and came from car engine. These samples were collected at the same time, from vehicles which had been lubricated with the same class of oil, but which did not necessarily have identical initial compositions.

Polyalphaolefin (PAO) is another common material for synthetic oil and it is not easily ionized by ESI. With sodium ions, PAO is observed in the sample as a dominant component.

Acknowledgments

This work is supported in part by the University of Maryland Baltimore, School of Pharmacy Mass Spectrometry Center (SOP1841-IQB2014).

References

1. Kilgour, D. P., Wills, R., Qi, Y. and O'Connor, P. B.: Autophaser: an algorithm for automated generation of absorption mode spectra for FT-ICR MS. Anal. Chem. **85**, 3903-3911 (2013)
2. Kilgour, D. P. A., Neal, M. J., Soulby, A. J. and O'Connor, P. B.: Improved optimization of the Fourier transform ion cyclotron resonance mass spectrometry phase correction function using a genetic algorithm. Rapid Commun. Mass Spectrom. **27**, 1977-1982 (2013)
3. Kilgour, D. and Van Orden, S.: Absorption mode FT-MS with no baseline correction. Submitted, (2015)
4. Kilgour, D. P. A., Mackay, C. L., Langridge-Smith, P. R. R. and O'Connor, P. B.: Appropriate Degree of Trust: Deriving Confidence Metrics for Automatic Peak Assignment in High-Resolution Mass Spectrometry. Anal. Chem. **84**, 7431-7435 (2012)
5. van Rooij, G. J., Duursma, M. C., Heeren, R. M. A., Boon, J. J. and de Koster, C. G.: High resolution end group determination of low molecular weight polymers by matrix-assisted laser desorption ionization on an external ion source Fourier transform ion cyclotron resonance mass spectrometer. J. Am. Soc. Mass Spectrom. **7**, 449-457 (1996)
6. Cho, Y., Witt, M., Kim, Y. H., Kim, S. H.: Characterization of crude oils at the molecular level by use of laser desorption ionization Fourier-Transform Ion Cyclotron resonance mass spectrometry. Anal. Chem. **84**, 8587-8594 (2012)
7. Kilgour D. P. A., Van Orden S. L., Tran B. Q., Goo Y. A. and Goodlett D.R.: Producing Isotopic Distribution Models for Fully Apodized Absorption Mode FT-MS. Anal. Chem. **In press** DOI: 10.1021/acs.analchem.5b01032

Posters from Goodlett Lab and Collaborators

MP073 UltrAWN-PTR-MS: Ultrasonic Acoustic Wave Nebulization coupled with Proton-Transfer-Reaction Mass Spectrometr, Lucas Maerk
MP076 Native MS using SAWN, a Novel Ionization Source for Waters SYNAPT G2, Gloria Yen
MP155 Bacterial Glycolipids Characterized on an IMS-QExactive, Yue Huang
MP180 Absorption Mode Analysis of FT-ICR Imaging Data Improves Peak Resolution in a Bordetella pertussis Infection Model, Alison Scott
MP217 Characterization of a Monoclonal Antibody (mAb) using Multiple Fragmentation Techniques and Novel FT Data Processing Software, Bao Tran
MP560 The Associations between Enterovirus Infections and Type 1 Diabetes, Niina Lietzen
MP646 Characterization of Semi-Synthetic Motor Oil using FT-ICR, Sung Hwan Yoon

TP018 Defining Limit of Detection of Mini Surface Acoustic Wave Nebulization Chip by Using Different Types of Mass Spectrometer, Tao Liang
TP122 Absorption Mode Gets Even Better with its Svelte New Curves, David Kilgour

WP233 Direct Beverage Analysis by SAWN MS, David Goodlett
WP268 A Cartesian Product Approach To Lipid A Structure Identification, Lisa Leung
WP450 Ultrasonic Acoustic Wave Nebulization-Mass Spectrometry (UltrAWN-MS) for Unconventional Explosives Characterization, Ben Oyler
WP475 Bridging the Gap between Ion Mobility Spectrometry and an Orbitrap, Mike Belov
WP595 Use of Native Mass Spectrometry for Quantification of Protein Complex, Wenjing Li

UNIVERSITY of MARYLAND SCHOOL OF PHARMACY