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nmRC CASE STUDY

PERFORMANCE FUEL ENGINEERING

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Performance Fuel Engineering

3D Orbitrap Secondary Ion Mass Spectrometry, XPS and AP-MALDI Case Study

Innospec Ltd.

Alterations to fuel specifications and increased stringency of emissions legislation leading to higher pressures of fuel injection and a more complex fuel mixture.

Increase in fuel system deposit formation issues from both engine manufacturers and fleet operators.

INJECTOR DEPOSITS

- Deposits commonly affects diesel and gasoline fuel injectors and filters.
- Lead to increased emissions poor efficiency and air quality.
- Need to understand key challenges…

❖ **What is their composition, origin and how do they form?**

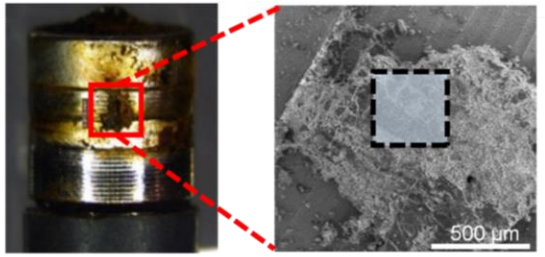
Clean injector

Fouled injector

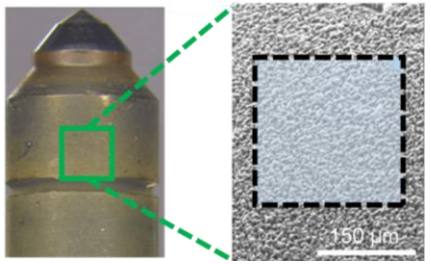
innospec specialty chemicals

Here we show *in-situ* analysis on three engine components:

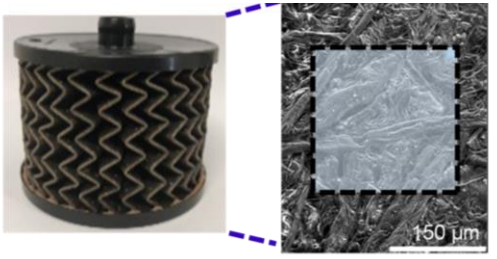
- Gasoline injector.



- Internal diesel injector.

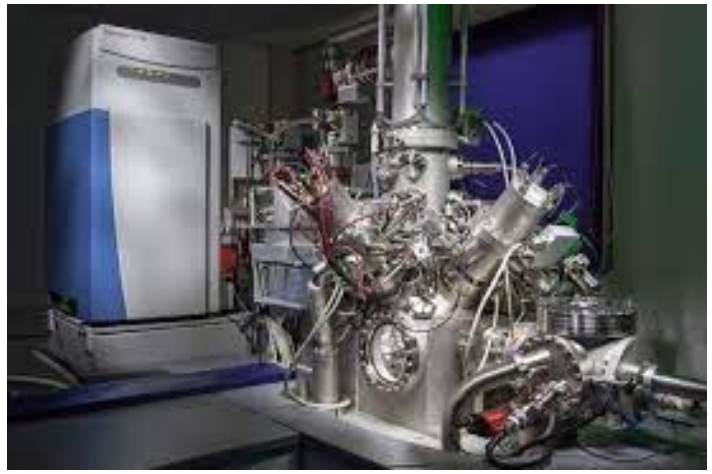


- Diesel filter.



ANALYSIS TECHNIQUES

3D OrbiSIMS - Sensitivity of SIMS with high mass resolution of Orbitrap™ analyser for 3D molecular analysis.

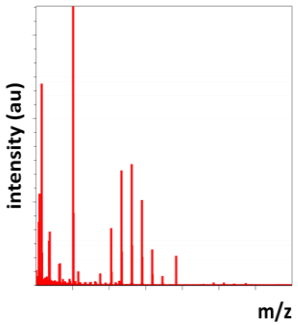


XPS – For accurate quantification of elemental data on deposits.

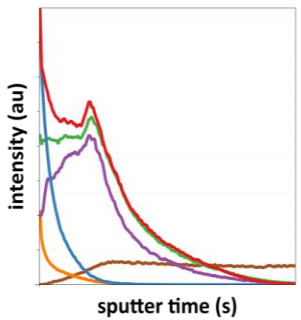
Analysis Techniques

MALDI-MS – Sensitive, *in-situ* MS analysis of samples up to very high masses. (*m/z* 2000)

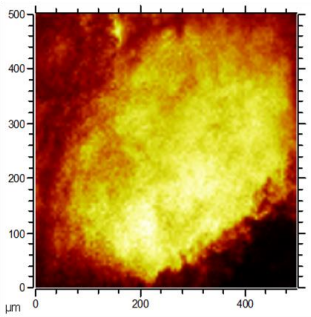
We acquired:



Spectra



Depth Profiles

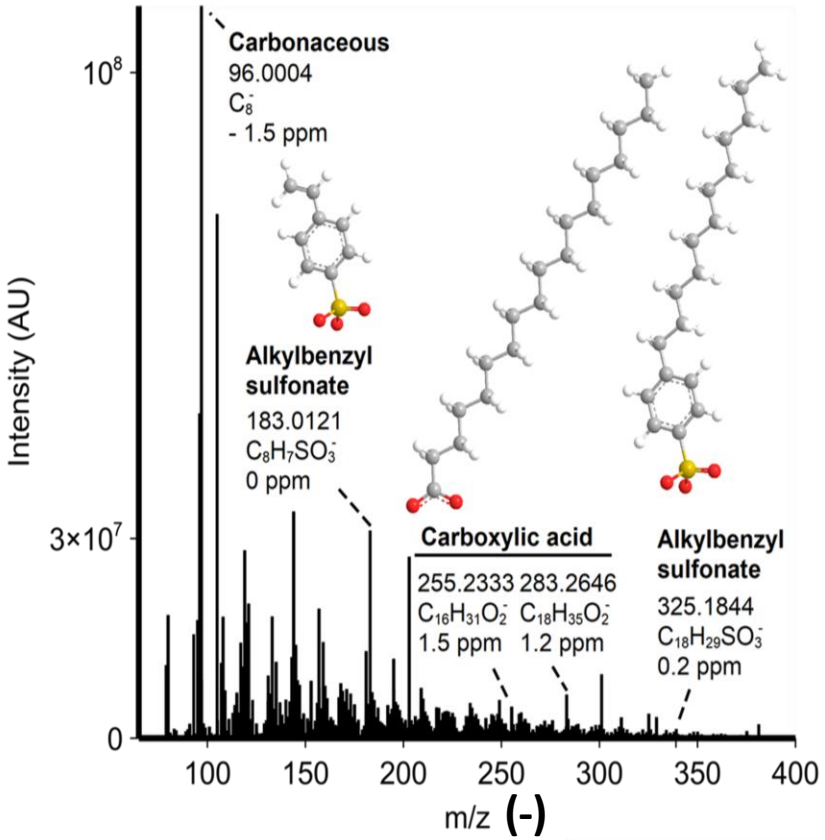


Chemical Images

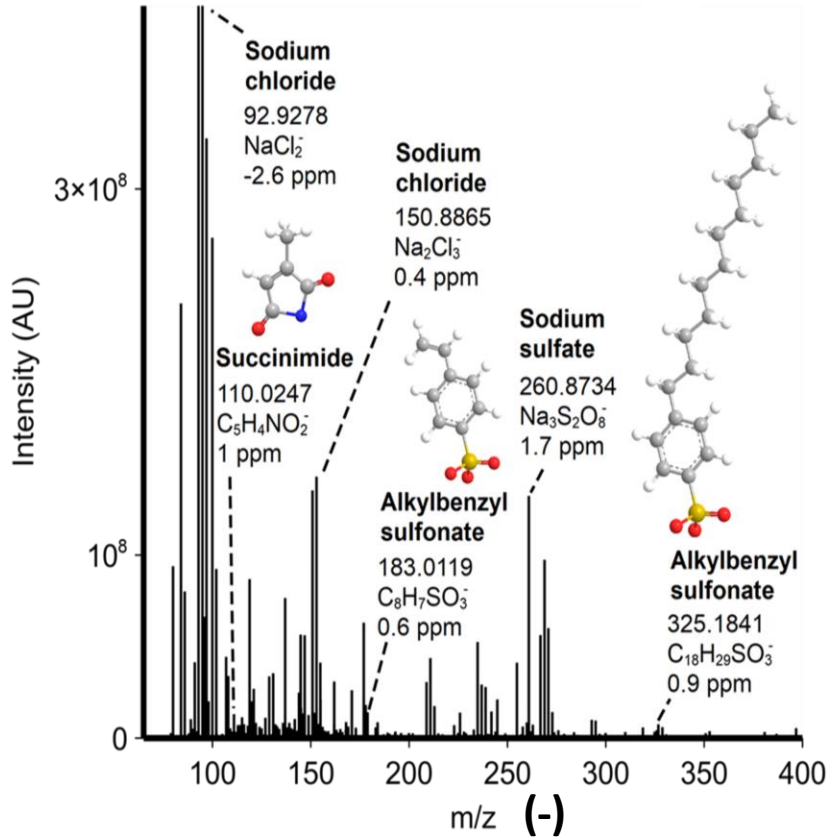
MS/MS – to confirm the assignments.

3D ORBISIMS SPECIATION OF MOLECULES

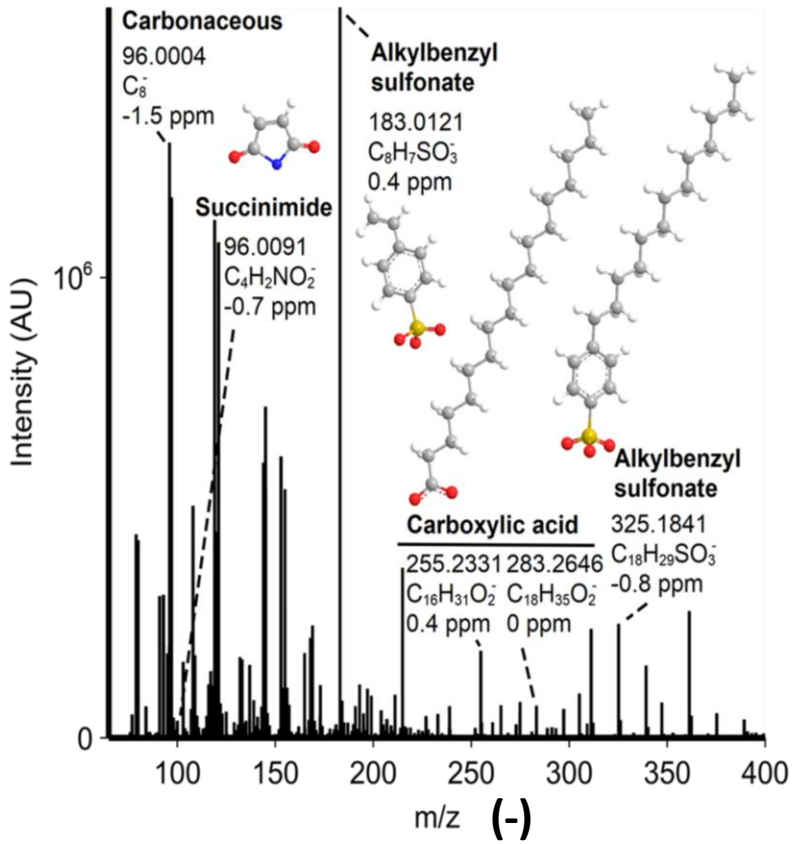
Gasoline Injector



Diesel Injector



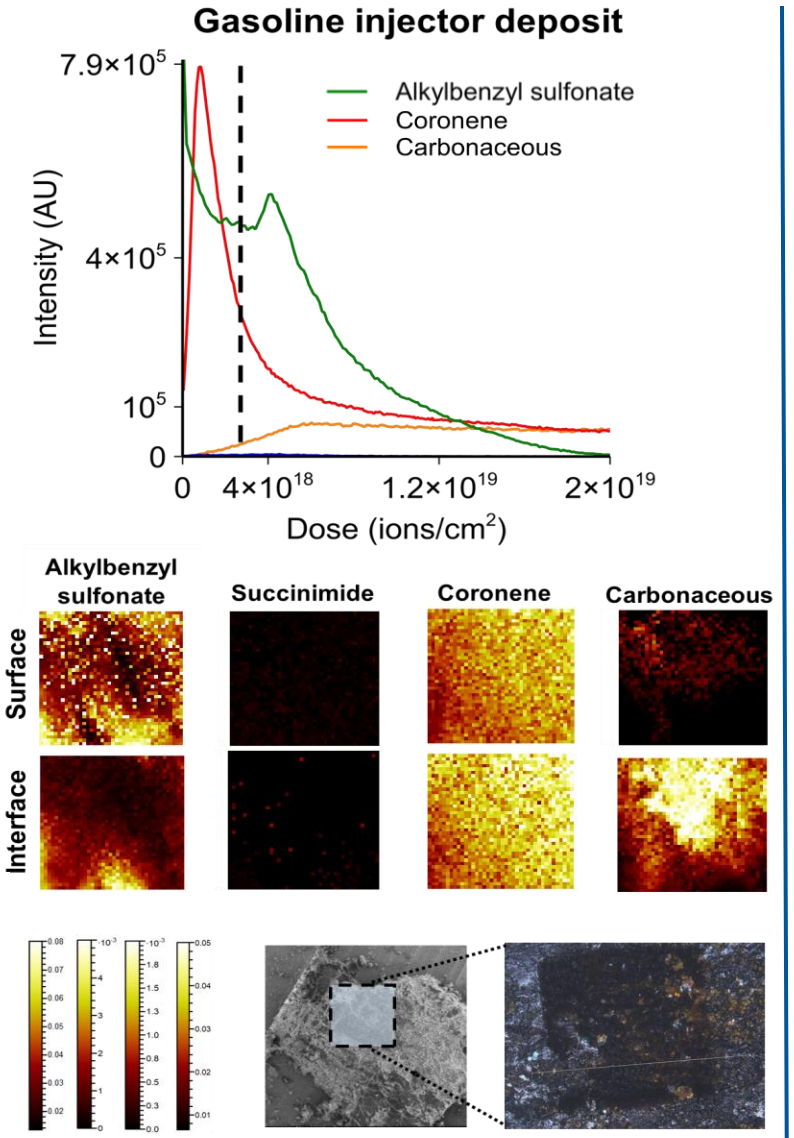
Diesel Filter

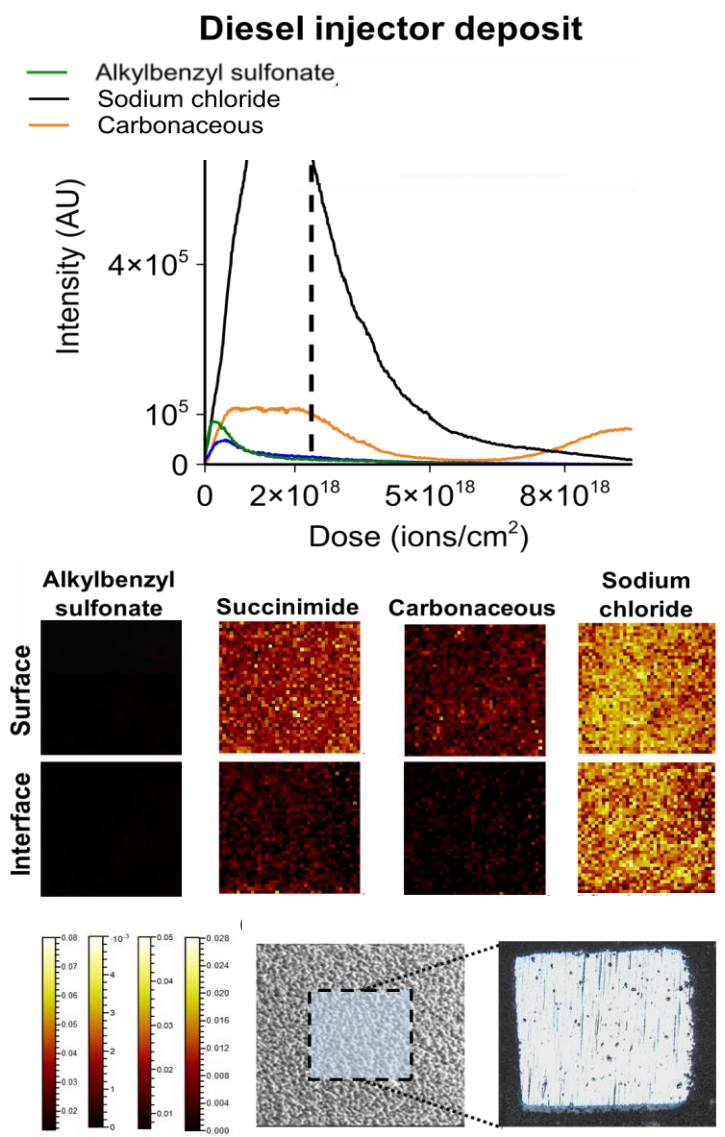


- Identification of molecular species and assignment of parent ions done *in-situ* (> *m/z* 1000 & < 2 ppm error).
- Lubricant oil derived sulfonates and linear carboxylic acids present in all samples.
- Sodium salt only in diesel samples. Sulfonate parent highest in filter.

3D ORBISIMS DEPTH PROFILES & IMAGES

- Depth profiling of deposits using the 3D OrbiSIMS allows an assessment of changing chemistry with depth.
- Fuel additive species demonstrated to be surface localised.
- Delocalized polycyclic aromatic hydrocarbons (PAHs) occupy the middle region in gasoline deposits.
- Localised carbonaceous ions showcased in gasoline deposits.
- Sodium chloride content dominates diesel deposits.

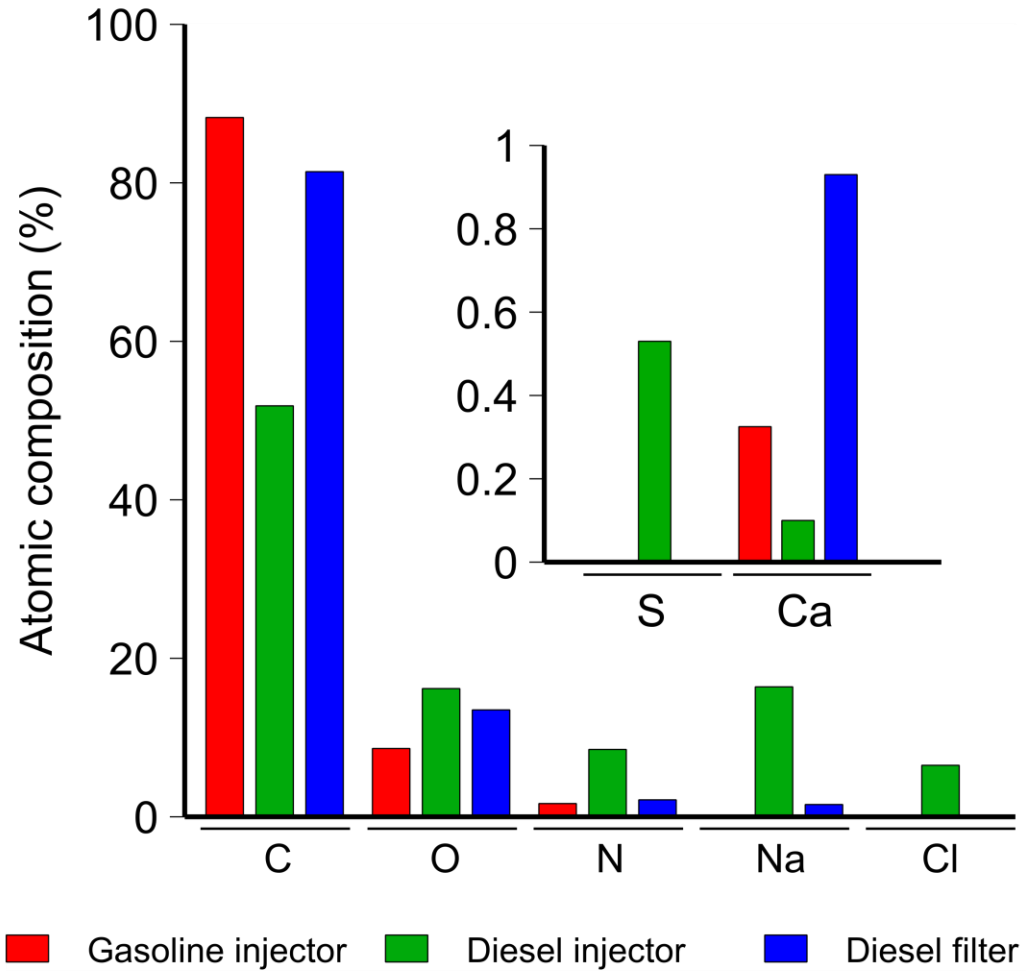




Edney, M. K. et al., ACS Appl. Mater. Interfaces, 2020.

QUANTIFICATION WITH XPS

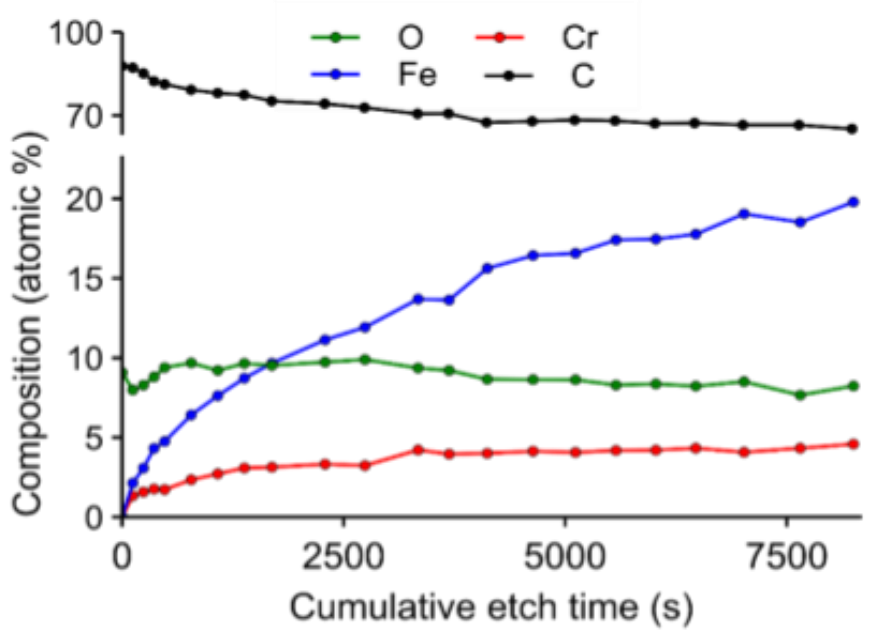
- XPS can accurately **quantify the elements** in a sample and assess **chemical state** (oxidation states etc.).
- A Kratos Axis ULTRA instrument was used to perform an elemental analysis after sample surface 'cleaning' with an Argon beam to remove opportunistic organic contaminants.
- High Na deposition was noted on the diesel injector deposits.
- Sulfates only seen on the diesel injector ($Na_3S_2O_8^-$, 0.4695 ppm).
- Sulfonates were seen to be trace contributors to all sample deposits.

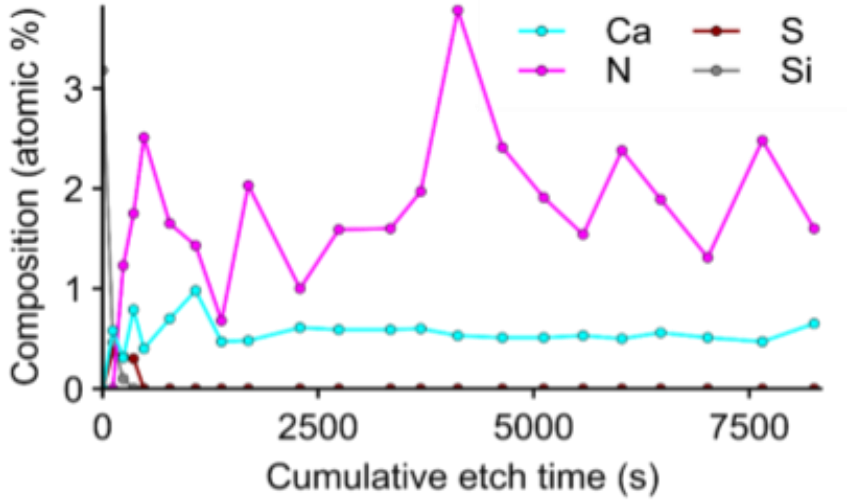


QUANTIFICATION WITH XPS

- The Kratos LIPPS instrument can generate **elemental depth profiles** by using an Argon sputter beam to remove surface material.

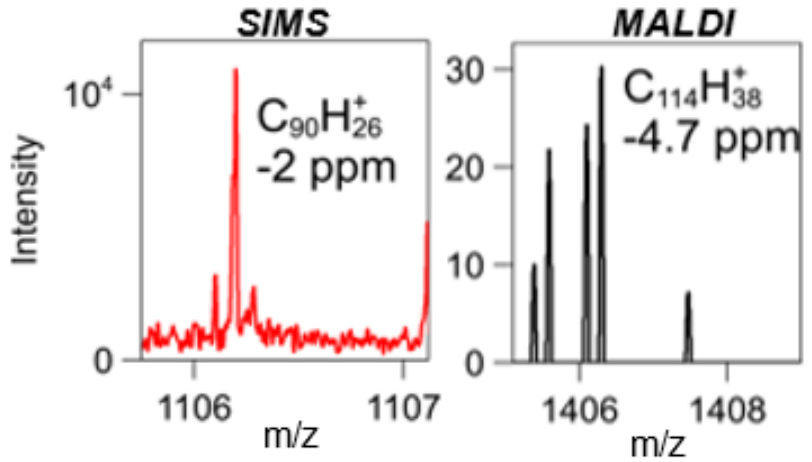
- Depth profiling results on the gasoline injector shows:
- High levels of C throughout the deposit.
- Surface contamination from Ca, S and S
- N increased and other species were surface localised.

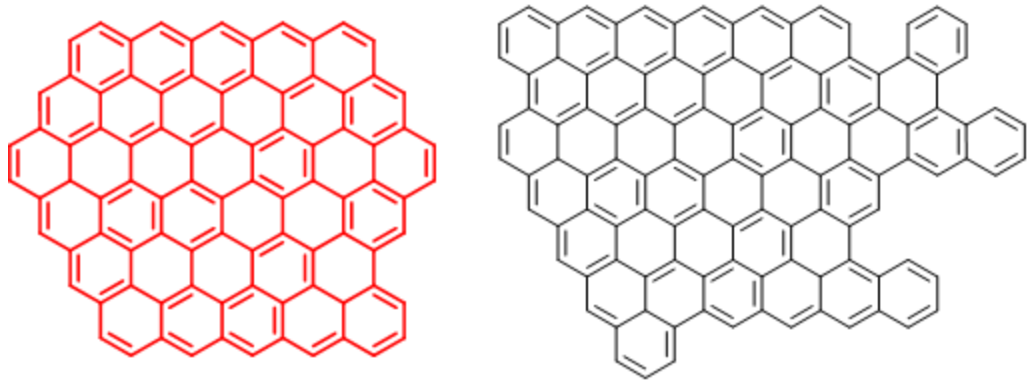




AP-MALDI Orbitrap MS

- Atmospheric pressure matrix assisted laser desorption ionization mass spectrometry (AP-MALDI MS) provides accurate **high mass** speciation *in-situ*.
- This is ideal for looking at parent molecular structures and was used to analyse gasoline deposits and compare the maximum mass of isolated species.
- Results show similar maximum masses of polyaromatic hydrocarbons – key deposit markers.
- Multi-technique approaches can help validate the results.





3D OrbiSIMS: $C_{90}H_{26}^+$

AP-MALDI: $C_{114}H_{38}^+$

Edney, M. K. et al., Analyst, 2020.

SUMMARY

- Fuel system deposit formations negatively affect engine performance and are not well characterised.
- 3D OrbiSIMS provides femtomolar mass sensitive (ppm) chemical analysis with depth through a surface and trap molecules > *m/z* 1000.
- Deposits found to be complex layered mixtures of carbon, polyaromatics, cycloalkanes, aromatics, straight chain and substituted alkanes, acids and inorganics.
- The better understanding of deposit formation is being used to develop strategies to prevent incidence with prospects of better engine wear and reduced environmental impact.

REFERENCES / ACKNOWLEDGEMENTS

For more details on the work showcased in this case study see the following publications:

Edney, M. K., Barker, J., Reid, J., Scurr, D. J. & Snape, C. E. Recent Advances in the Analysis of GDI and Diesel Fuel Injector Deposits. *Fuel* **272**, 117682 (2020).

Edney, M. *et al.* Spatially Resolved Molecular Compositions of Insoluble Multilayer Deposits Responsible for Increased Pollution from Internal Combustion Engines. *ACS Applied Materials & Interfaces* **12**, 51026–51035.

The Orbitrap Secondary Ion Mass Spectrometry and XPS analysis documented here was performed in the Nanoscale and Microscale Research Centre. AP-MALDI was performed in the Advanced Materials and Healthcare Technologies research group of the School of Pharmacy at the University of Nottingham.

ADDITIONAL INFORMATION

- We hope the information provided in this case study is of interest.
- If you wish to get in touch with us to discuss any of the information provided, raise a query/concern or provide feedback then please use any of the methods listed below:

nmRC Commercial Services
Nanoscale & Microscale Research Centre
University Park
Nottingham
NG7 2RD

Telephone: **+44(0)115 951 5046**
Email: nmcs@nottingham.ac.uk
Fax: **+44 (0)115 846 7969**
Website: **www.nottingham.ac.uk/nmrc-commercial**