

EVALUATING THE NOVEL UNISPRAY IONISATION SOURCE FOR THE ANALYSIS OF PETROLEUM SAMPLES

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INTRODUCTION

A novel UniSpray[®] ionisation source has been developed that uses a unique approach to generating ions for mass spectral analysis. This atmospheric pressure ionisation source comprises a grounded capillary from which analyte solution elutes that is nebulized by high velocity nitrogen gas (Figure 1).¹ The eluent spray impacts on a cylindrical, stainless steel target rod held at high voltage, typically ~0.5 - 4.0 kV, offering the potential to ionise analytes with greater efficiency. In this work, ions produced by UniSpray ionisation are compared with ions produced by electrospray (ESI), atmospheric pressure chemical ionisation (APCI), atmospheric pressure photoionisation (APPI), and the atmospheric solids analysis probe (ASAP) ionisation sources for a range of petroleum related samples.

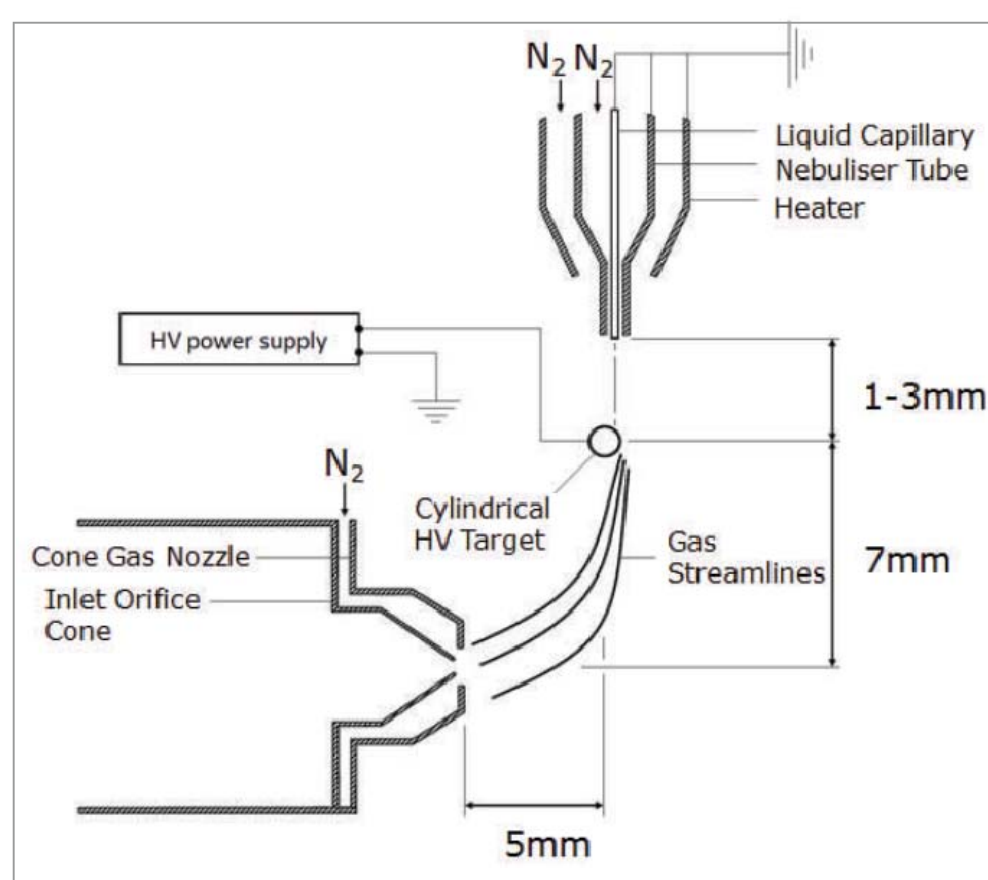


Figure 1. Schematic of the UniSpray ionisation source showing source geometry and gas flow

METHODS

The ionisation process in UniSpray utilises the Coandă effect whereby a flow of particles (gaseous or liquid) bend round a curved surface. Figure 2 shows the UniSpray source *in situ* on the mass spectrometer, a close up of the inside of the source, and the Coandă effect in action.

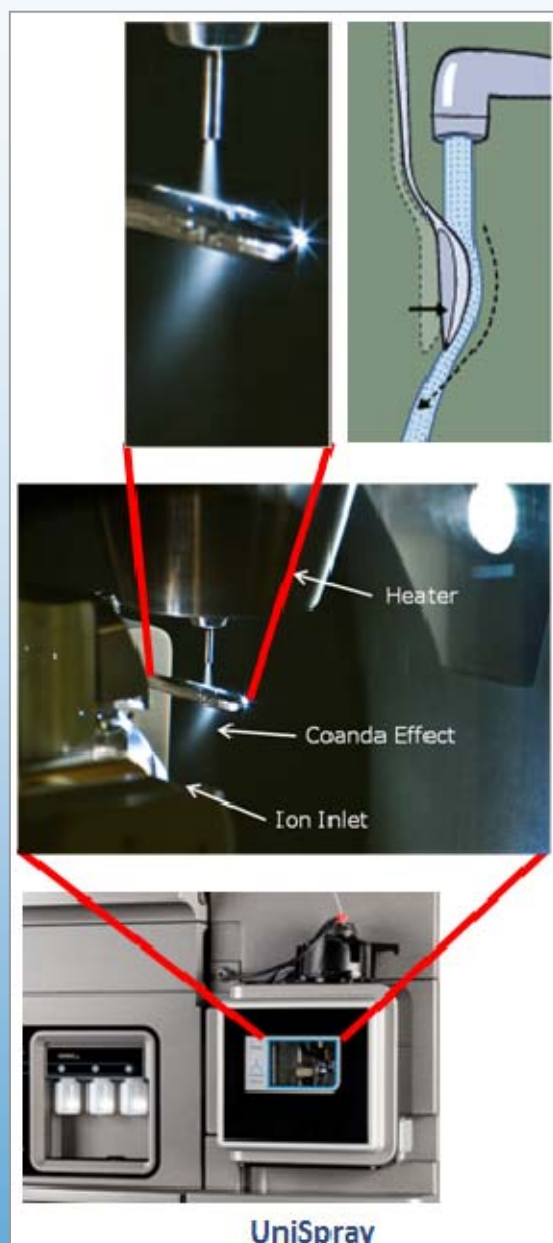


Figure 2. The UniSpray source *in situ* (lower image), a close up of the inside of the UniSpray source (middle image), photograph of the Coandă effect occurring in the ionisation source and a cartoon illustration of the Coandă effect (upper image)

The work shown in this poster was carried out using direct infusion or thermal desorption analysis (ASAP) coupled with a SYNAPT G2-Si HDMS mass spectrometer, with the exception of the oilfield additives work that was carried out using UHSFC (UPC²) separation coupled with a Xevo TQD tandem quadrupole mass spectrometer.

RESULTS & DISCUSSION

Initially, the UniSpray spectra were compared to the typical spectra achieved when using ESI, APPI, APCI, and ASAP. Figure 3 shows examples of spectra acquired using each of these ionisation sources for the analysis of a Safaniya vacuum residue (VR).

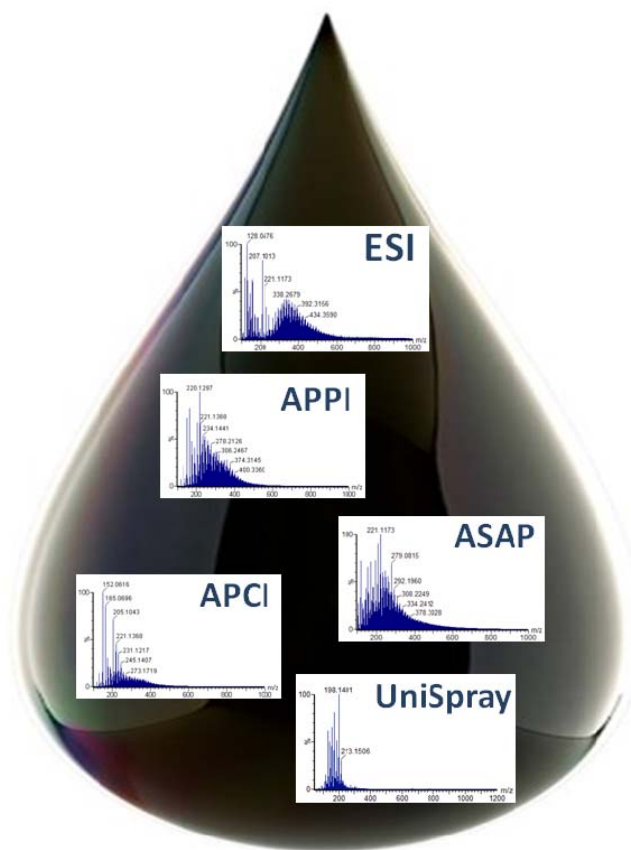


Figure 3. Representative full spectra acquired for a Safaniya VR sample using UniSpray and four different alternative ionisation sources

It should be noted that the UniSpray analysis was done more than a year after the original analyses so it is likely that the sample had degraded. Work by Nascimento, *et al.* demonstrated that UniSpray offered greater coverage of diesel components than other ionisation sources²—but that was not observed here.

When optimising conditions for the analysis of the Safaniya VR sample it was noted that the response was dependent upon the precise impact point of the eluent onto the impactor rod surface.

This phenomenon is illustrated in Figure 4. For the Safaniya VR, the response increased when the spray impact point was closer to the centre of the impactor rod and decreased as it was moved to the right-hand side of the impactor rod.

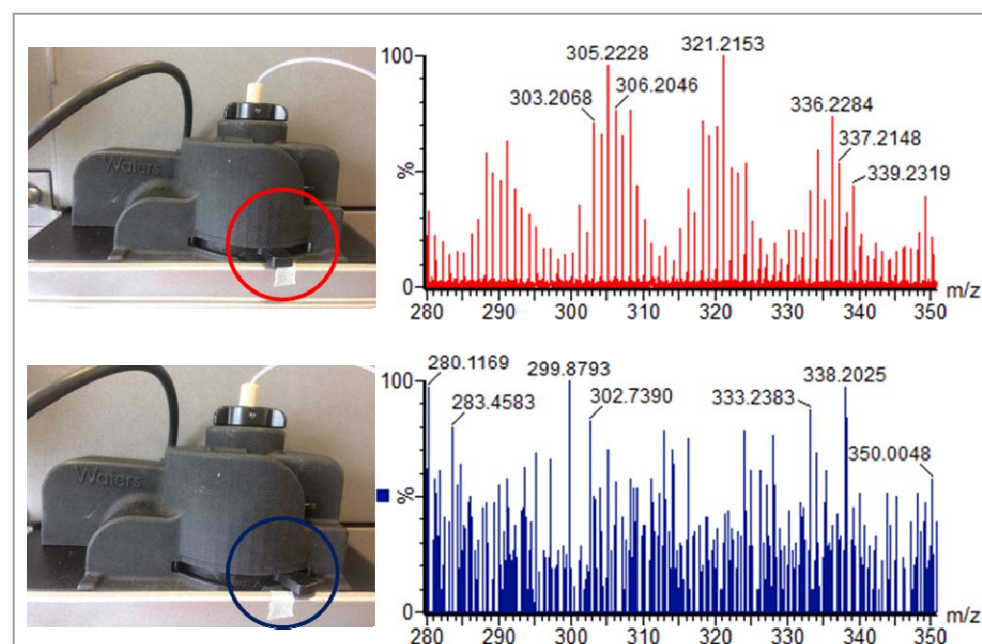


Figure 4. Response for the Safaniya VR sample was dependent upon the impact point of the spray on the impactor rod. When positioned to the far right (lower image and blue spectrum) the response was poor. When positioned towards the middle (upper image and red spectrum) the response increased significantly. All other conditions were identical between the two acquisitions

The voltage applied to the impactor rod also had a significant effect on the appearance of the spectra obtained. In Figure 5, the spectra acquired for an Arabian Light VR are shown. Two different impactor rod voltages were used, 2.0 kV and 4.0 kV. The 4.0 kV acquisition showed greater ion intensity than the 2.0 kV acquisition.

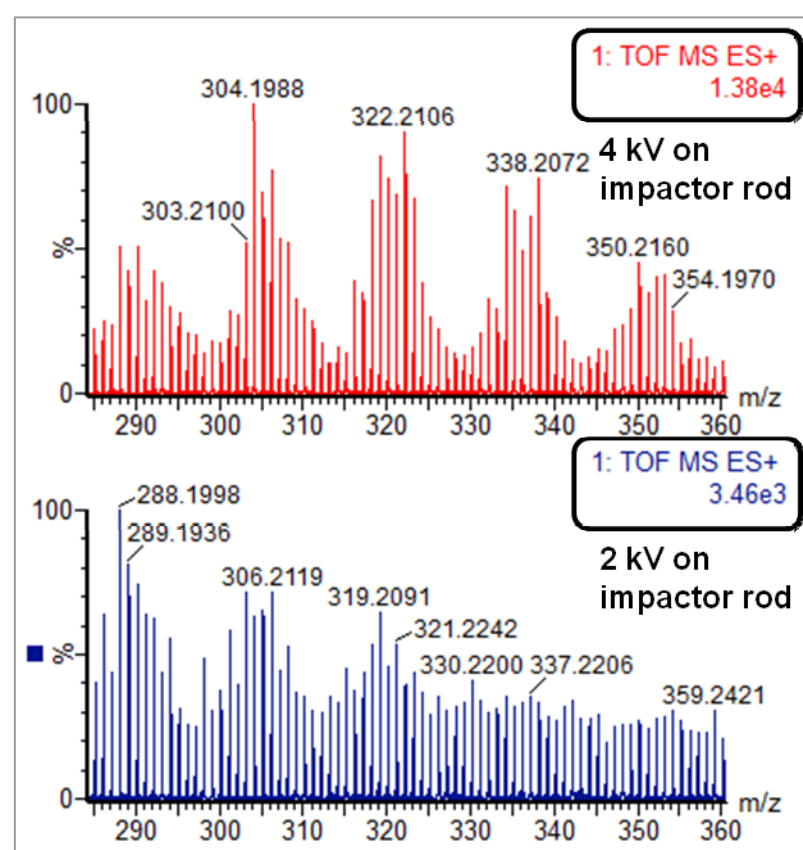


Figure 5. Spectra for an Arabian Light VR sample acquired at different impactor rod voltages. 2.0 kV on the impactor rod produced lower intensity ions (lower, blue spectrum) and 4.0 kV on the impactor rod produced higher intensity ions (upper, red spectrum)

RESULTS & DISCUSSION

A mix of typical PAH compounds was also analysed by the same five ionisation sources. Figure 6 shows a magnified region of the spectra obtained. This shows that, under the conditions used for this analysis, UniSpray is not applicable for ionising PAH compounds. As would be expected, APPI is the optimal ionisation technique for analysing PAHs.

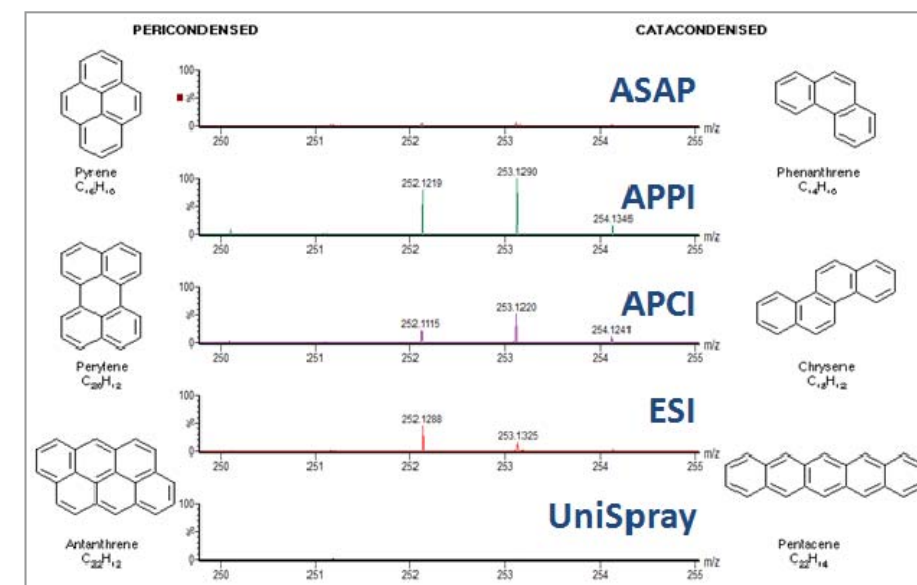


Figure 6. Magnified regions of spectra acquired for a PAH compound mix using each different ionisation source

A selection of imidazole and quaternary ammonium salt oilfield chemicals were analysed quantitatively by UHPLC-MS/MS using ESI and UniSpray ionisation sources. The calibration curves for a 21OH imidazole compound are shown in Figure 7 and the calibration curves for a C12 quaternary ammonium salt are shown in Figure 8.

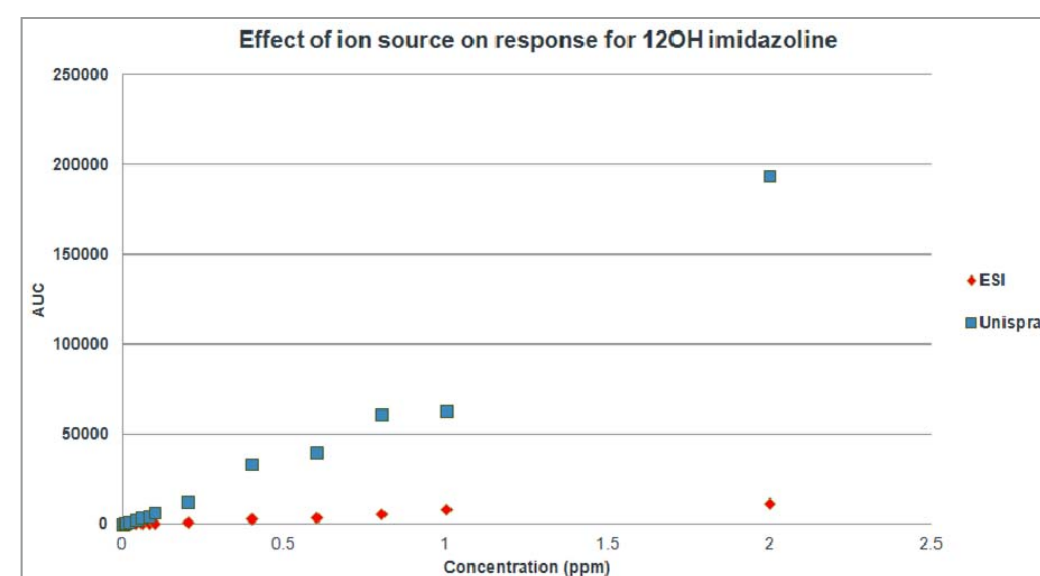


Figure 7. Calibration curves for a 21OH imidazole compound analysed by ESI (red diamonds) and UniSpray (blue squares)

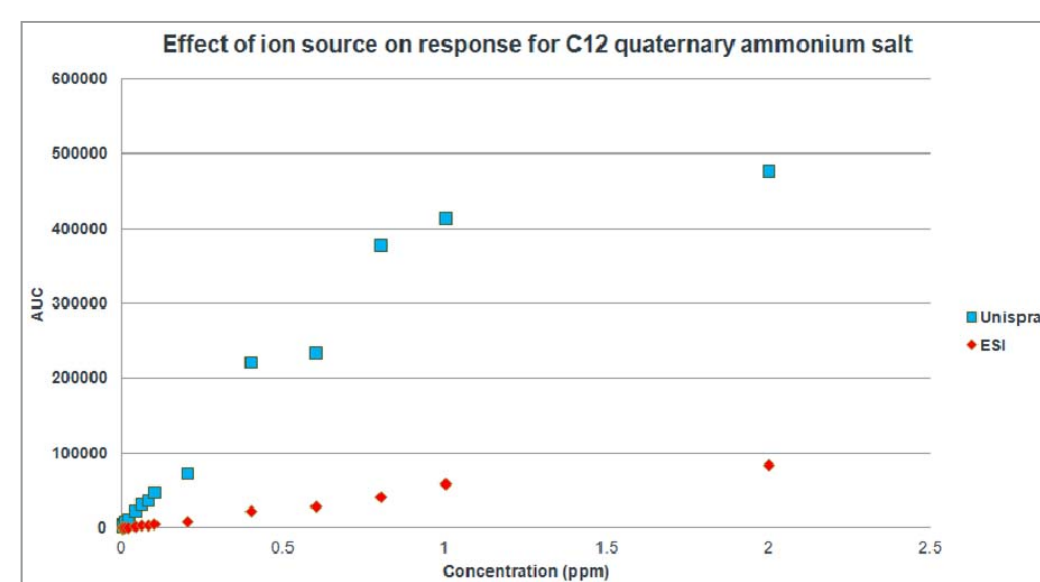


Figure 8. Calibration curves for a C12 quaternary ammonium salt compound analysed by ESI (red diamonds) and UniSpray (blue squares)

The focused comparison of UniSpray with ESI for the analysis of oilfield additive chemicals revealed a very large improvement in response when using UniSpray compared with ESI. A similar result was observed by Lubin and co-workers in a head-to-head comparison of ESI and UniSpray for the analysis of eicosanoid compounds.³

CONCLUSION

- UniSpray showed a significant improvement in response compared with ESI for the analysis of selected oilfield chemicals
- Careful optimisation of key UniSpray parameters, such as impactor rod voltage and spray position, is necessary for the analysis of crude oil fractions
- UniSpray is a valuable additional component in the "tool box" available to mass spectrometrists to address sample diversity
- Other complementary ionization techniques, such as ASAP and APPI, are also required to ensure the maximum coverage of the most challenging samples

Acknowledgements

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References

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