

COMPARISON OF THE NOVEL UNISPRAY ION SOURCE TO A RANGE OF ALTERNATIVE ATMOSPHERIC PRESSURE IONIZATION SOURCES

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INTRODUCTION

A novel UniSpray[®] ionization source has been developed that uses a unique approach to generating ions for mass spectral analysis (Figure 1).^{1,2} This atmospheric pressure ionization source comprises a grounded capillary from which analyte solution elutes that is nebulized by high velocity nitrogen gas. 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 ionize analytes with greater efficiency. In this work, ions produced by UniSpray ionization are compared with ions produced by ESI, APCI, APPI, and ASAP ionization sources for a range of small molecules, including PAHs, pesticides, and polymer additives.

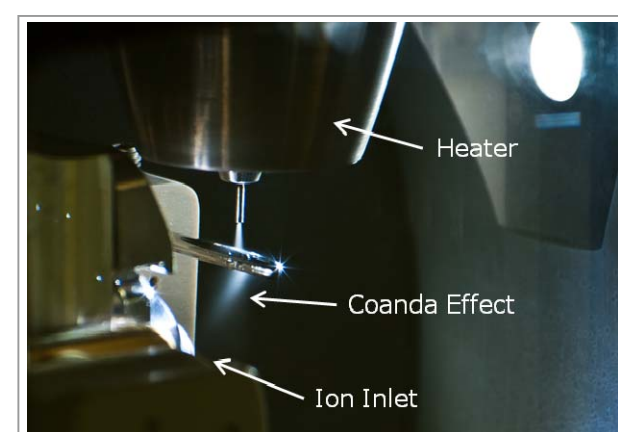


Figure 1. Internal view of the UniSpray ionization source

METHODS

- Solvent standard solutions were prepared at suitable analytical concentrations using appropriate solvents: ~0.1 - 1.0 µg/mL for the small molecules mixes, ~0.1% for the engine oils, and ~1 mg/mL crude oil samples.
- UniSpray responses were evaluated at three different impactor target rod voltages: 0.5 kV, 1.0 kV, and 3.0 kV
- APCI responses were evaluated at four different corona currents: 1 µA, 5 µA, 10 µA, and 12 µA
- ASAP responses were evaluated at two different corona currents: 1 µA, and 12 µA
- High resolution mass spectral data, with ion mobility, were acquired using a SYNAPT G2-Si HDMS instrument and reviewed in MassLynx v.4.1 software.

SYNAPT G2-Si HDMS conditions:

- Cone voltage: 50 V
- Source temperature: 120 °C
- IMS Wave velocity: 1000 m/s (fixed)
- IMS Wave height: 40 V
- IMS cell pressure: 3.3 mbar

METHODS

- All data were acquired by combining sample solutions with representative mobile phases—either 1:1 MeOH:H₂O, 100% MeOH, or 1:1 MeOH:Toluene—depending on the ionization technique under consideration or the classes of compounds being analysed.
- A separate evaluation was also carried out specifically looking at the response of oilfield additives analysed by ESI and UniSpray
- A C12 quaternary ammonium salt and a 12OH imidazoline compound were separated using a UHPSFC system coupled to a tandem quadrupole MS

UHPSFC conditions:

- Solvent A: supercritical CO₂
- Solvent B: MeOH + 2% H₂O + 50 mM ammonium acetate
- Column: ACQUITY HSS C18 SB, 1.8 µm, 3.0 x 100 mm
- Temperature: 40 °C
- Pressure: 150 bar
- Injection volume: 2 µL
- Gradient table (Table 1):

Time (min)	Flow rate (mL/min)	%A	%B
0	1.50	100	0
2.0	1.50	60	40
2.3	1.50	60	40
4.0	1.50	100	0

Type of Samples	Example Compound	Molecular Formula	Relative Monoisotopic Mass	Structure
Pesticides	Thiabendazole	C ₁₀ H ₇ N ₃ S	201.0361	
PAHs	Benzo [a] fluoranthene	C ₂₀ H ₁₂	252.0939	
Cosmetics & Allergens (mix 1)	Sulfadimethoxine	C ₁₂ H ₁₄ N ₄ O ₂ S	310.0736	
FAMES	Methyl heptacosanoate	C ₂₂ H ₄₄ O ₂	340.3341	
Cosmetics & Allergens (mix 2)	UV 328 (Tinuvin 328)	C ₂₂ H ₂₈ N ₂ O	351.2311	
Engine Oil	Oil additive (4-Nonyl-N-(4-nonylphenyl) aniline)	C ₃₀ H ₄₂ N	421.3709	
Polymer Additives	Uvitex OB	C ₂₆ H ₂₈ N ₂ O ₂ S	430.1715	
OLEDs	Ir(Fppy) ₃	C ₃₃ H ₁₈ F ₆ IrN ₃	761.1011	

Table 2. Example representative compounds for each small molecule mix. Also analysed was a Safaniya vacuum residue petroleum sample (not illustrated in table)

RESULTS & DISCUSSION

Table 2 shows a summary of the small molecule mixtures used for this work and includes an example representative compound for each mixture.

To illustrate the performances of the different ionization sources with different classes of compounds, axes linked spectra were generated. Figure 2 shows a zoomed region of the mass spectra acquired from analysis of an organic light emitting diode (OLED) mix of compounds. The illustrative compound of interest forms an isotopic cluster of ions around *m/z* 762. UniSpray showed the most intense absolute response with APCI and ASAP producing almost similarly intense responses.

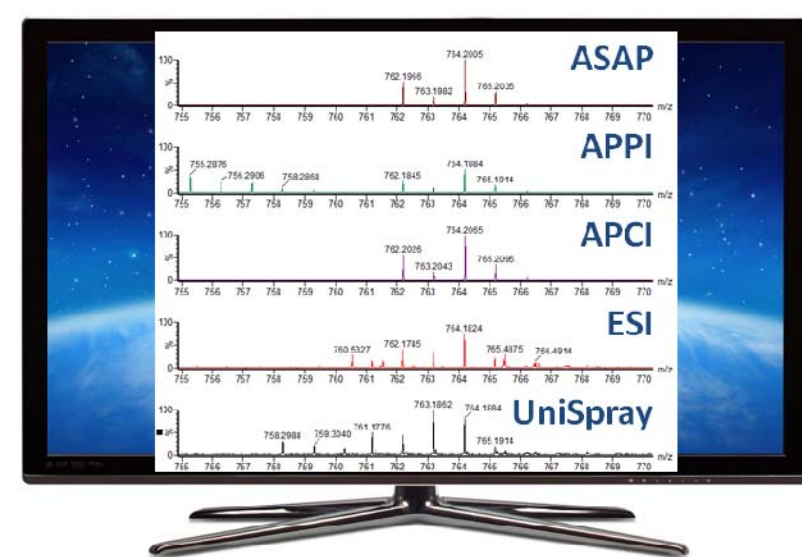


Figure 2. Zoomed regions of spectra acquired for the OLED compound mix using each different ionization source

Figure 3 shows a similar zoomed region of the mass spectra acquired from analysis of a polycyclic aromatic hydrocarbon (PAH) mix of compounds. The illustrative compound of interest forms an isotopic cluster of ions around *m/z* 252 since these compounds typically form radical cations. Interestingly, ESI is able to ionize the compound whereas UniSpray shows little to no response. APPI produced the most intense response with APCI showing a similar ion pattern but less intense and ASAP showing little to no response.

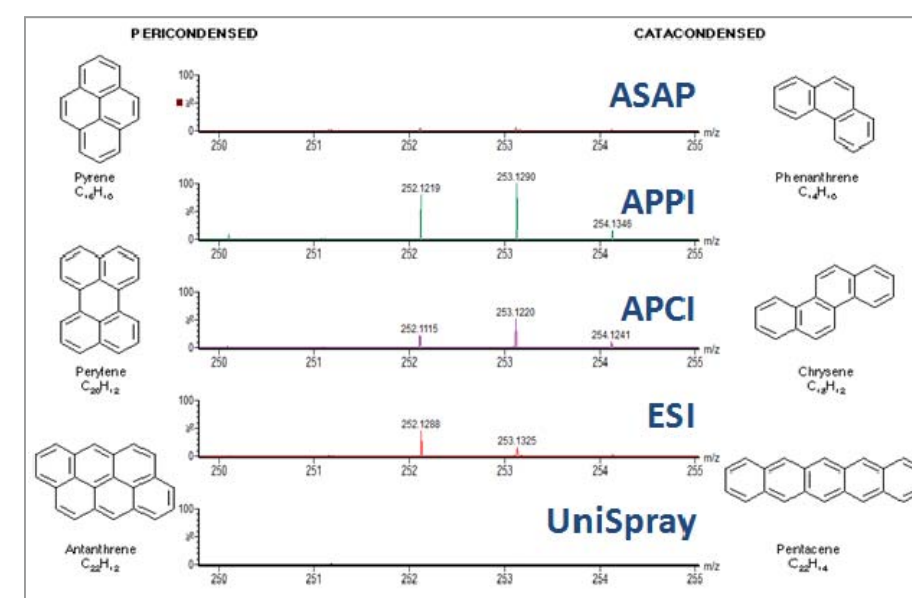


Figure 3. Zoomed regions of spectra acquired for the PAH compound mix using each different ionization source

The Safaniya vacuum residue petroleum sample was analysed using direct infusion. Figure 4 illustrates the full spectra acquired with each ionization source. Here we can see the value of having different ionization techniques available to ensure comprehensive coverage of such a complex sample.

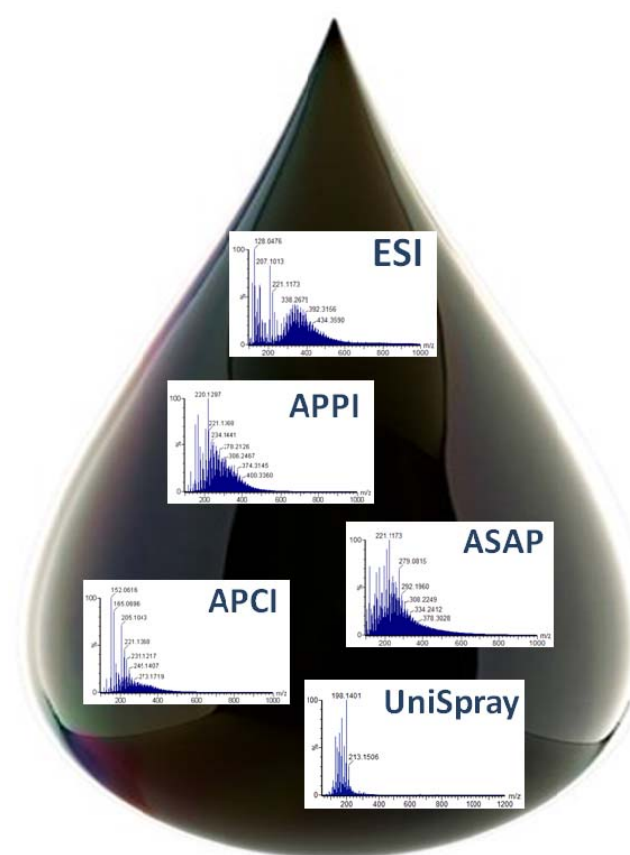


Figure 4. Full spectra acquired for the Safaniya vacuum residue sample using each different ionization source

Table 3 shows a summary of the results for one particular group of compounds—the polymer additives mix. It can be seen from the yellow highlighted results that UniSpray produced the best response for most of the compounds in this mix

It was also noted that the optimal impactor rod voltage depended upon the type of adduct being formed. Protonated species gave a better response with a higher applied voltage (e.g. 3.0 kV), whereas sodiated species gave a better response with a lower applied voltage (e.g. 0.5 kV). This phenomenon is illustrated further in Figure 5. Axes linked spectra for two of the polymer additives, Uvitex OB and Irganox 245, are shown. Uvitex OB favours ion formation via protonation and Irganox 245 favours ion formation via sodiation. The differing responses for different applied impactor rod voltages can clearly be seen.

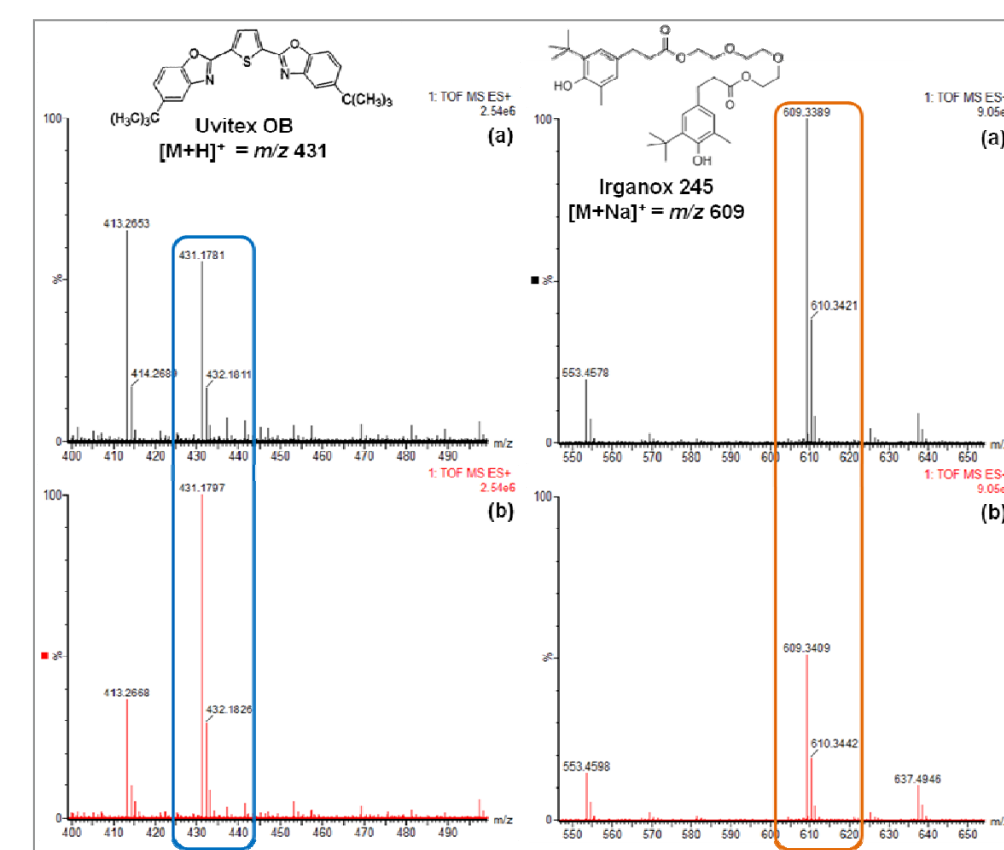


Figure 5. Spectra for protonated Uvitex OB and sodiated Irganox 245. Upper spectra labelled (a) have 0.5 kV applied to the impactor rod lower spectra labelled (b) have 3.0 kV applied to the impactor rod

Name	Formula	Relative Monoisotopic Mass (m/z)	APCI+		APPI+		ESI+		US+	
			Ion Observed	Ion Intensity (arb. unit)	Ion Observed	Ion Intensity	Ion Observed	Ion Intensity	Ion Observed	Ion Intensity (kV on rod)
Diethyl phthalate	C ₁₂ H ₁₄ O ₄	222.0892	X	X	X	X	[M+Na] ⁺	2.91e5	[M+Na] ⁺	1.09e5 (0.5 kV)
Tinuvin P	C ₁₃ H ₁₁ N ₃ O	225.0902	[M+H] ⁺	1.92e6 (1 µA)	[M+H] ⁺	1.35e6	[M+H] ⁺	1.41e6	[M+H] ⁺	2.01e6 (3.0 kV)
Dibutyl sebacate	C ₁₈ H ₃₄ O ₄	314.2457	X	X	X	X	[M+Na] ⁺	1.10e6	[M+Na] ⁺	5.72e6 (0.5 kV)
Diphenyl phthalate	C ₂₀ H ₁₄ O ₄	318.0892	X	X	X	X	[M+Na] ⁺	4.24e5	[M+Na] ⁺	3.17e6 (0.5 kV)
2-hydroxy-4-octyloxy benzophenone	C ₂₁ H ₂₆ O ₃	326.1882	[M+H] ⁺	1.47e5 (1 µA)	[M+H] ⁺	2.06e5	[M+H] ⁺	3.45e5	[M+H] ⁺	4.47e5 (3.0 kV)
Tinuvin 327	C ₂₀ H ₂₄ CIN ₃ O	357.1606	[M+H] ⁺	1.07e6 (1 µA)	[M+H] ⁺	1.25e6	[M+H] ⁺	1.03e6	[M+H] ⁺	8.62e5 (3.0 kV)
TCP	C ₂₁ H ₂₁ O ₄ P	368.1177	[M+H] ⁺	2.04e5 (1 µA)	[M+H] ⁺	2.80e5	[M+H] ⁺	1.29e6	[M+Na] ⁺	3.33e6 (0.5 kV)
Uvitex OB	C ₂₆ H ₂₈ N ₂ O ₂ S	430.1715	[M+H] ⁺	1.46e5 (1 µA)	[M+H] ⁺	2.10e5	[M+H] ⁺	1.58e6	[M+H] ⁺	2.54e6 (3.0 kV)
Cyasorb 2908	C ₃₁ H ₅₄ O ₃	474.4073	[M+H] ⁺	4.79e4 (1 µA)	[M+H] ⁺	4.74e4	[M+H] ⁺	1.15e5	[M+Na] ⁺	1.03e5 (0.5 kV)
Irganox 1076	C ₃₅ H ₆₂ O ₃	530.4695	[M+H] ⁺	5.80e3 (1 µA)	M+	6.32e4	[M+Na] ⁺	5.86e5	[M+Na] ⁺	1.94e6 (0.5 kV)
Irganox 245	C ₃₄ H ₅₀ O ₈	586.3506	[M+Na] ⁺	1.21e4 (1 µA)	[M+H] ⁺	1.43e4	[M+Na] ⁺	1.46e6	[M+Na] ⁺	5.99e5 (0.5 kV)
Irganox 1098	C ₄₀ H ₆₄ N ₂ O ₂	636.4866	[M+H] ⁺	3.24e4 (1 µA)	[M+H] ⁺	5.18e4	[M+Na] ⁺	5.92e5	[M+Na] ⁺	4.36e5 (0.5 kV)
Tinuvin 360	C ₄₁ H ₅₀ N ₆ O ₂	658.3995	[M+H] ⁺	2.02e5 (1 µA)	[M+H] ⁺	2.13e5	[M+H] ⁺	4.91e5	[M+H] ⁺	3.50e5 (0.5 kV)
Ethanol 330 (Irganox 1330)	C ₅₄ H ₇₈ O ₃	774.5951	[M+H] ⁺	9.04e3 (1 µA)	M+	1.97e4	[M+Na] ⁺	4.47e4	[M+Na] ⁺	3.23e4 (0.5 kV)
Uvinul 3030	C ₅₉ H ₄₈ N ₄ O ₈	1060.3472	X	X	X	X	[M+Na] ⁺	6.72e3	[M+Na] ⁺	1.01e4 (0.5 kV)
Irganox 1010	C ₇₃ H ₁₀₈ O ₁₂	1176.7841	X	X	X	X	[M+Na] ⁺	8.81e3	X	X

Table 3. Summary of responses for the polymer additives mix comparing the responses of the four liquid flow ion sources. The yellow highlighted values indicate the best responses and hence the best ionization technique for each compound

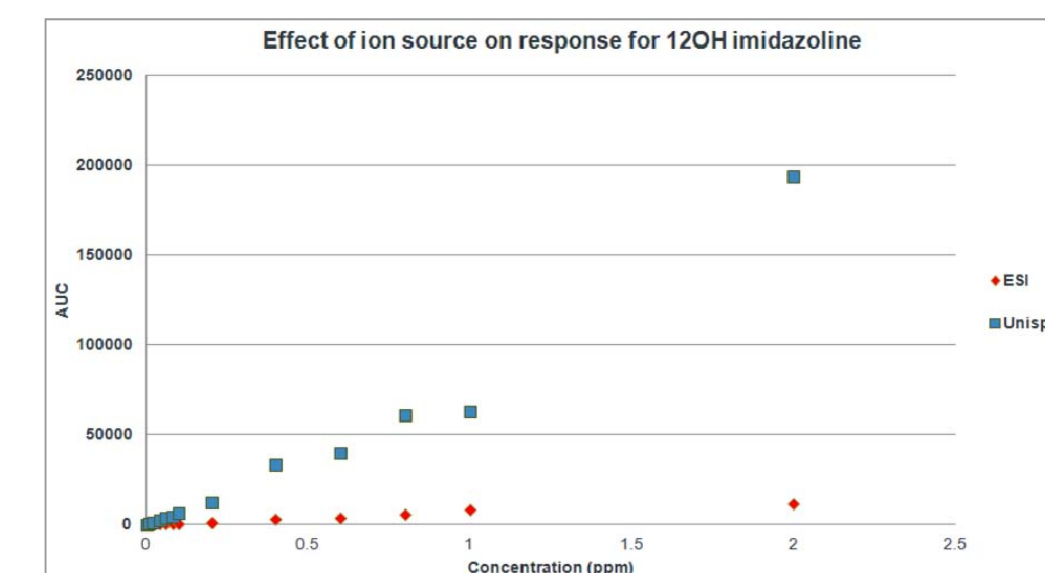


Figure 6. Calibration curves for a 21OH imidazoline compound analysed by ESI (red diamonds) and UniSpray (blue squares)

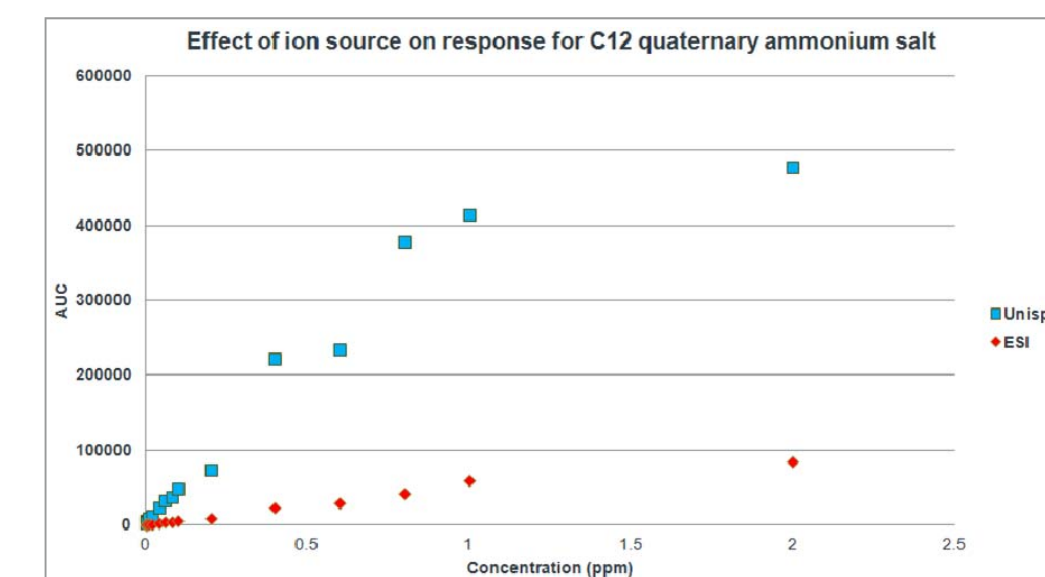


Figure 7. Calibration curves for a C12 quaternary ammonium salt compound analysed by ESI (red diamonds) and UniSpray (blue squares)

The focussed 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.

Figure 6 shows the calibration curves for a 12OH imidazoline additive and Figure 7 shows the calibration curve for a C12 quaternary ammonium salt.

Both compounds were analysed over the concentration range 10 ppt to 2 ppm. In the case of the 12OH imidazoline, UniSpray offered up to a 17-fold increase in response and for the C12 quaternary ammonium salt up to a six-fold increase in response was observed.

Key structural features of any analyte can indicate which ionization technique might be suitable for that analyte. Some of these structural features are summarized in Table 4.

Ion Source	Appropriate Structural Characteristics	Example Compounds/Classes
UniSpray or ESI	Polar molecules, e.g. containing oxygen or nitrogen atoms, hydroxyl groups, amine groups, carboxyl groups, etc. that can form ions in solution	Pesticides, e.g. tebuconazole, thiabendazole Veterinary drugs, e.g. flubendazole, oxolinic acid
APCI or ASAP	Non-polar species particularly with non-aromatic ring structures	Steroids, e.g. 17 α -hydroxyprogesterone Biocidal compounds, e.g. tributyltin chloride Phytosterols, e.g. campesterol
APPI or ASAP	Non-polar aromatic species or species with regions of delocalized electron density. Species with chromophores	PAHs, e.g. pyrene, anthracene Vitamin B12 UV stabilizers, e.g. Tinuvin compounds
ASAP	Some saturated species	Low molecular weight poly(ethylene) FAMES, e.g. methyl heptacosanoate

Table 4. Summary of some key structural features that make a molecule amenable to ionization by a particular ionization source

CONCLUSION

- UniSpray has been demonstrated to have broad applicability across several classes of compounds but it is not necessarily the best ionization source for all molecules
- UniSpray is a valuable additional component in the “tool box” available to mass spectrometrists to address sample diversity
- Other complementary ionization techniques, such as APCI and APPI, are also required to ensure the maximum coverage of the most challenging samples
- UniSpray was observed to have differing impactor rod optimized voltages depending on the adduct formed by the analyte of interest (sodiated vs. protonated)
- UniSpray showed a significant improvement in response compared with ESI for the analysis of selected oilfield chemicals
- A molecule's structural and functional characteristics can influence the choice of the most suitable ionization technique

Acknowledgements

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References

- Bajic, S., An Aerodynamic Perspective on Impactor API Sources, Waters Poster No. PSTR134897766, presented at ASMS 2016.
- Lubin, A.; Geerinckx, S.; Bajic, S.; Cabooter, D.; Augustijns, P.; Cuyckens, F.; Vreeken, R. J. J. *Chromatog. A* 2016, 1440, 260.