

Unispray™ ion source coupled to UHPSFC for the detection of oilfield additives

Efstathios Andreas Elia¹, William Durnie², Ed Sprake³ and G. John Langley¹

¹Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton; ²BP Exploration, Sunbury-on-Thames, Middlesex;

³Waters Corporation, Wilmslow, UK

Introduction

- The oil and gas industry relies on the use of carbon steel for transmission pipelines which is susceptible to corrosion
- Use of corrosion inhibitors is the most cost effective means of corrosion mitigation
- Although beneficial to the industry, these additives are toxic and pose a direct threat to aquatic life
- Ongoing need to accurately quantify such additives in trace concentrations in oilfield fluids
- Quantitation of such CIs has been shown to be achieved by direct analysis of crude oil using UHPSFC¹
- A novel ion source (Unispray™) was compared to standard ESI source for the trace level detection of six corrosion inhibitors in various oilfield fluids

Experimental

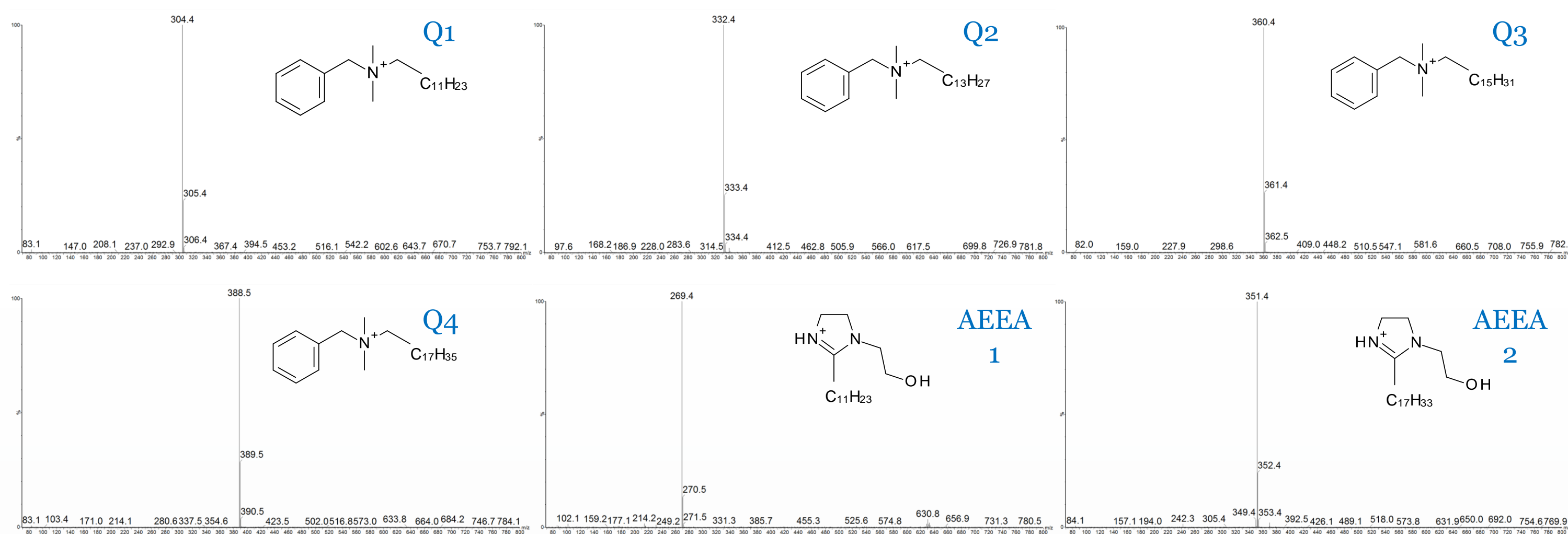


Figure 1. Positive ion ESI mass spectra and chemical structures for each CI used.

- Quaternary amines readily amenable to (+)ve ion ESI due to permanent charge, M⁺ ion detected
 - AEEA imidazolines also easily protonated through the addition of formic acid, [M + H]⁺ ion detected
 - Full scan mass spectra acquired for concentrations above 1 ppm, SRM spectra acquired for concentrations below 1 ppm
- UHPSFC conditions used**
- Instrument: Waters Acquity UPC²
- Mobile phase A: scCO₂
- Mobile phase B: MeOH + 2% H₂O + 50 mM NH₄OAc
- Flow rate: 1.5 mL/min.
- Column: Acquity HSS C18 (100 mm × 3 mm, 1.8 μm)

- UHPLC conditions used**
- Instrument: Waters Acquity UPLC H-class
- Mobile phase A: H₂O + 0.2% formic acid
- Mobile phase B: ACN + 0.2% formic acid
- Flow rate: 0.7 mL/min.
- Column: Acquity BEH C18 (100 mm × 3 mm, 1.7 μm)

Mass spectrometer conditions used

Parameters	ESI	Unispray™
Cone Voltage	20 V	20 V
Capillary Voltage	3.3 kV	1.4 kV
Source temp.	150 °C	150 °C
Desolvation temp.	350 °C	350 °C
Desolvation gas flow	700 L/h	700 L/h
Extractor	3 V	3 V

Results and Discussion

Design of Unispray™ source

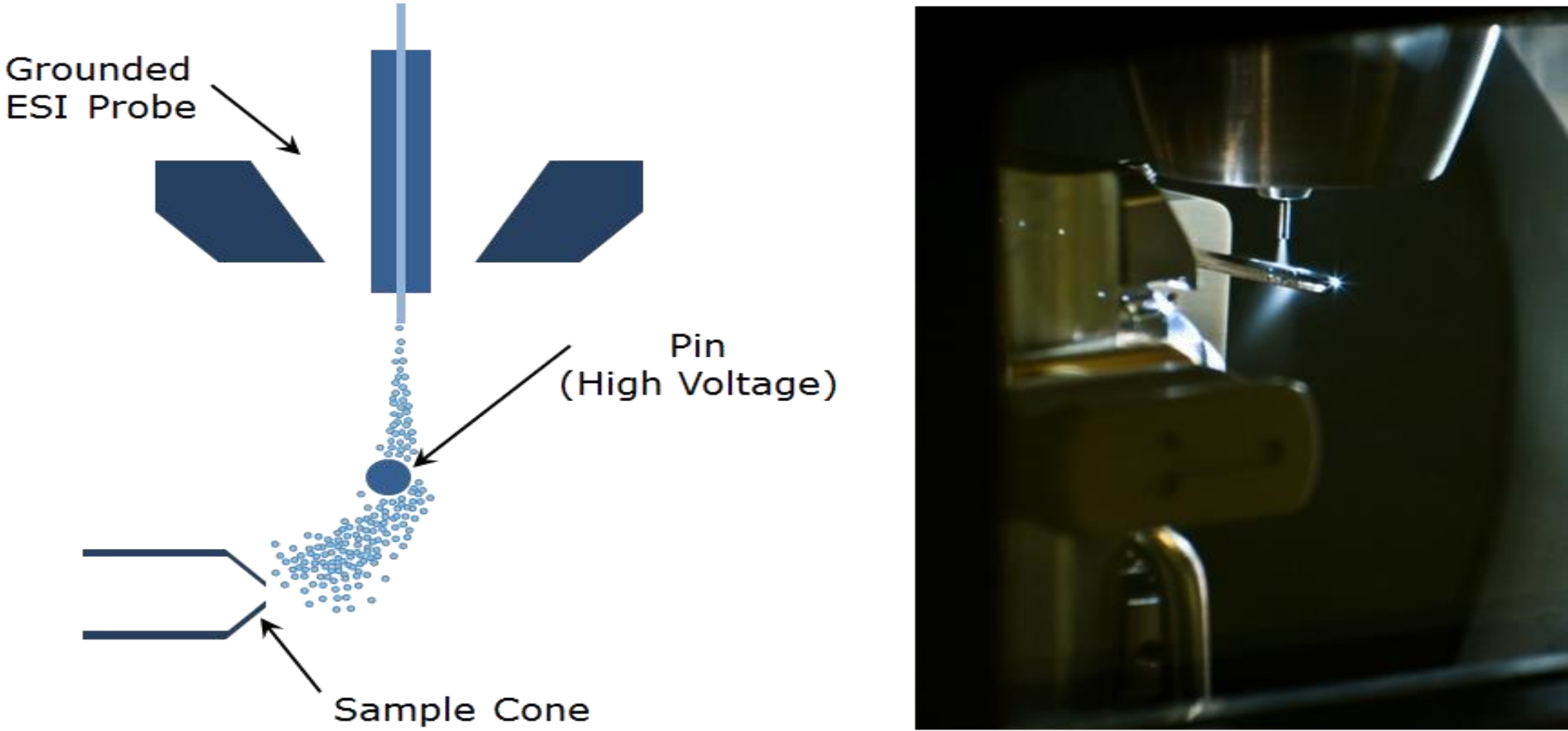


Figure 2. Schematic representation and actual photograph of the Unispray™ source .

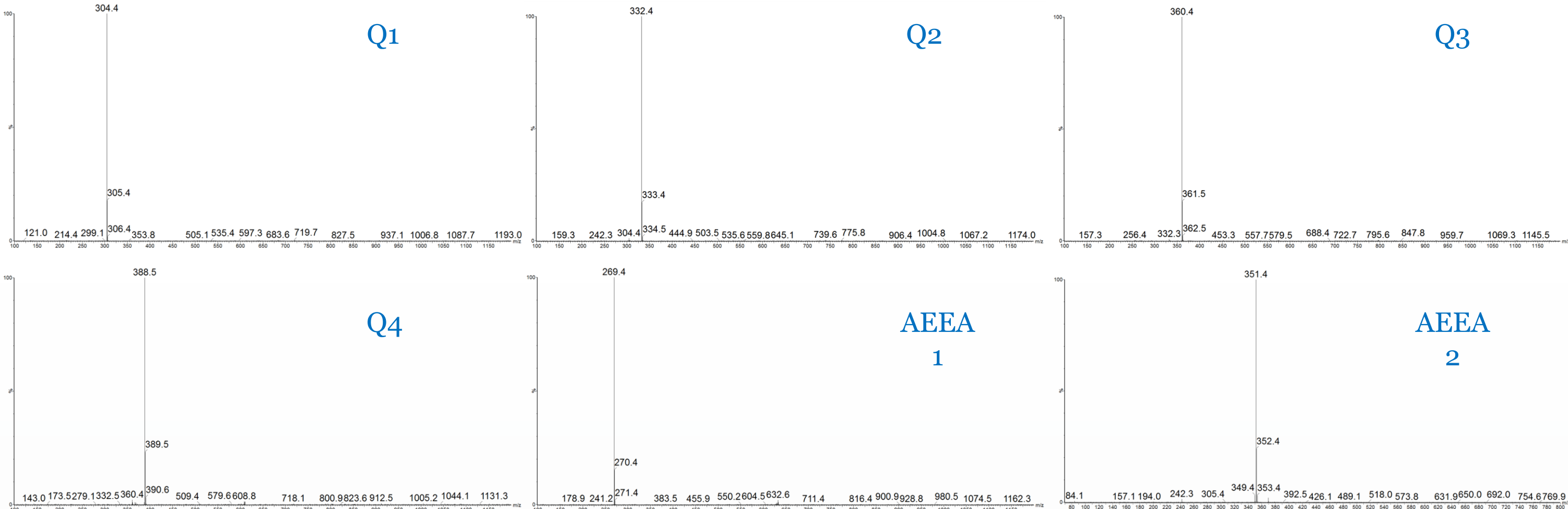


Figure 3. Positive ion Unispray™ mass spectra for each CI used.

Comparison of UHPSFC to UHPLC

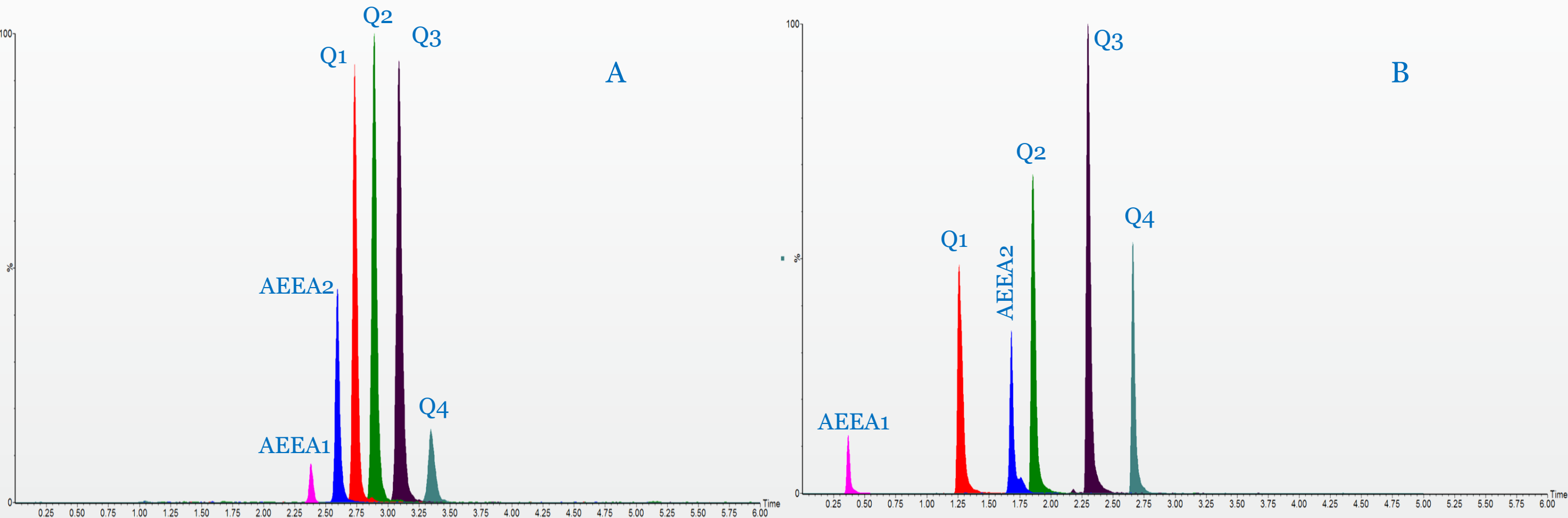


Figure 3. Combined RICCs of a 10 ppm solution of the model CI formulation and analysed using UHPSFC (A) and UHPLC (B).

One quaternary amine and one imidazoline were chosen as model CIs to perform all statistical analyses on. The observations below are true for all other CIs in the formulation.

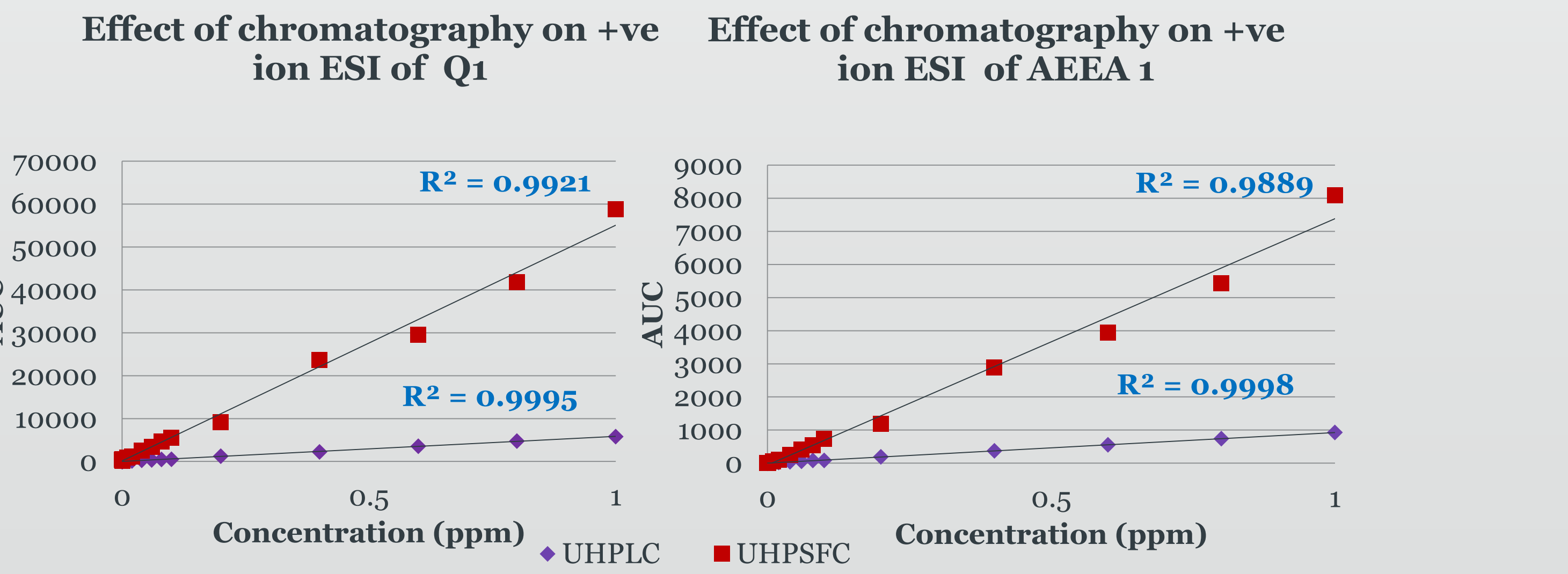


Figure 4. A comparison of the ESI response of two CIs using UHPSFC and UHPLC.

Results and Discussion

Comparison of ESI and Unispray™ using UHPLC

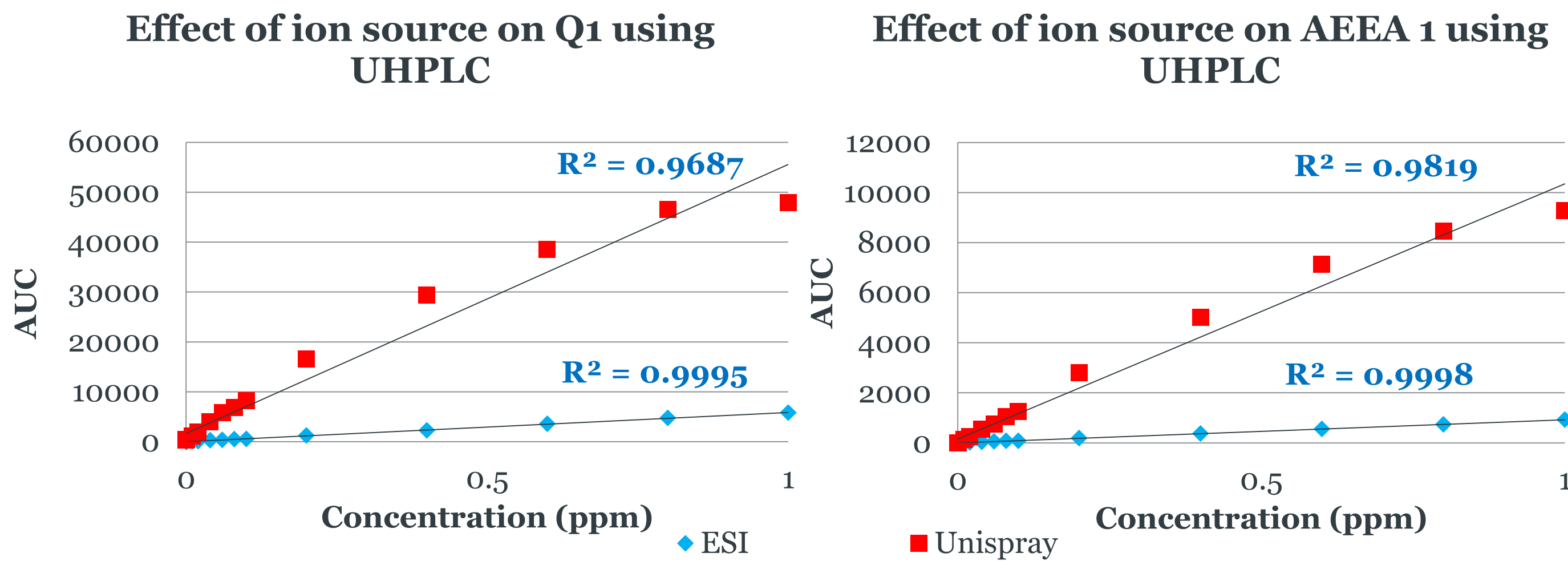


Figure 5. Comparison of the MS response for the two model CIs using UHPLC with Unispray™ and ESI.

Comparison of ESI and Unispray™ using UHPSFC

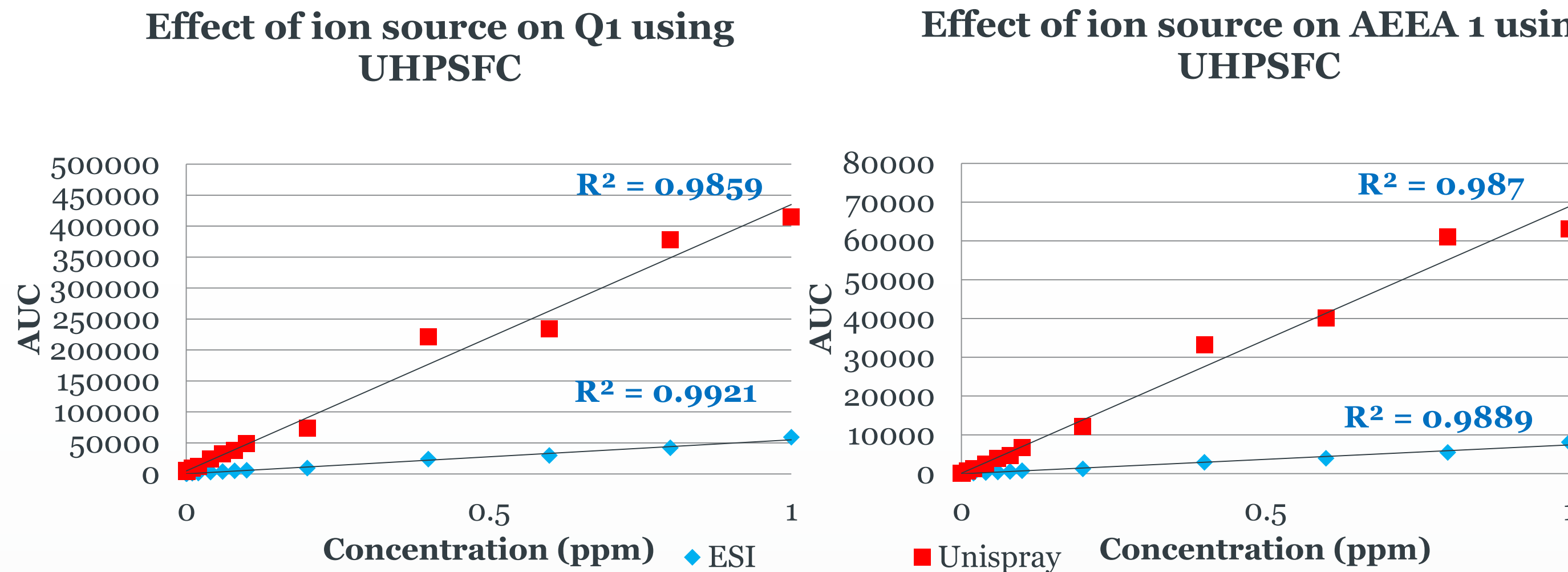


Figure 6. Comparison of the MS response for the two model CIs using UHPLC with Unispray™ and ESI.

Using Unispray™ ion source with UHPSF is shown to increase the MS response by a factor of 60-100 when compared to UHPLC with ESI. This is believed to be due to the formation of smaller droplets in early stages of ESI or the introduction of the impact pin directs more of spray towards the MS or even that it produces a finer electrospray plume.

Conclusions

- Chromatographic separation of six CIs used in the oil industry achieved in 6 min. with no sample preparation required
- UHPSFC provides a 6-fold increase in sensitivity compared to UHPLC²
 - Unispray™ ion source introduces a 6 to 10-fold increase when compared to standard ESI
- A combination of UHPSFC and Unispray™ could provide a 60 fold increase in sensitivity compared to using UHPLC with ESI
- Experimentation with the Unispray™ ion source and different chemistries can provide further insight into the ionisation mechanism of both ESI and Unispray™

References

- Elia Efstathios, Durnie William, Langley G. John, Determination of oilfield additives using separation science and mass spectrometry, BMSS Annual Meeting, 2015
- Lucie Nováková, Alexandre Grand-Guillaume Perrenoud, Raul Nicoli, Martial Saugy, Jean-Luc Veuthey, Davy Guillarme, Ultra high performance supercritical fluid chromatography coupled with tandem mass spectrometry for screening of doping agents. I: Investigation of mobile phase and MS conditions, Analytica Chimica Acta, Volume 853, 1 January 2015, Pages 637-646

Acknowledgements



Waters
THE SCIENCE OF
WHAT'S POSSIBLE.™

EPSRC
Engineering and Physical Sciences
Research Council