

Introduction

Samples ionisation in the absence of high voltage has been observed when interfacing SFC to an ESI source, with some compounds showing increased sensitivity with the source high voltage turned off. In this study an attempt is made to probe this ionisation phenomenon and quantify the improved sensitivity by studying a series of test compounds. Regardless of the source of this ionisation process, the increased sensitivity in the absence of high voltage can help in lowering the limit of detection for such compounds.

Experimental Setup

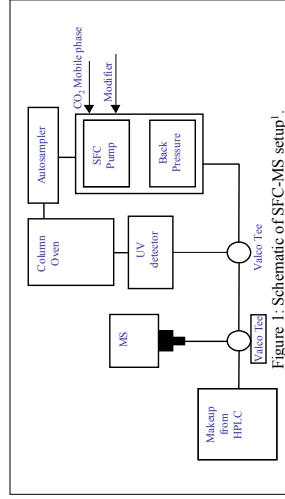


Figure 1: Schematic of SFC-MS setup¹.

Experimental Approach

- ESI compared to APCI
- Charged residue model?²
- Thermospray?³
- HPLC vs SFC?⁴
- Sonic spray ionisation^{3,4}
 - Pressure changed
 - Modifier % changed
 - Nebulisation gas

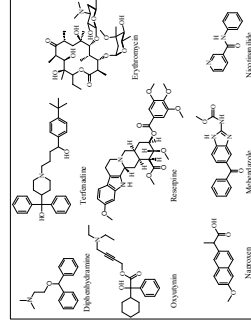


Figure 2: Structures of test compounds.

Results and Discussion

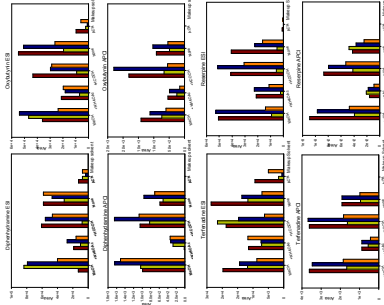
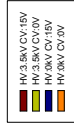
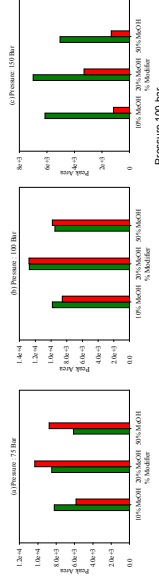


Figure 3: ESI & APCI comparison for the four standards.

- The ESI data showed
- Improved ionisation in absence of high voltage
 - Ionisation suppressed with addition of ammonium acetate
 - Formic acid does not enhance ionisation
 - APCI data comparable with ESI data



Effect of Pressure and Modifier



- Mixture of terfenadine, oxycodone and erythromycin analysed at varying pressure and modifier percentage
- Pressure 100 bar and modifier 30% MeOH Optimum conditions for maximum sensitivity in presence or absence of high voltage

Figure 4: Plots showing pressure and modifier effects. Structures for the standards used

Acetonitrile, Methanol Modifier

Increased ionisation with MeOH modifier compared to MeCN

Indicating the ionisation efficiency dependent on the volatility of the solvent⁵.

Sensitivity

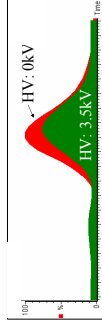


Figure 6: Base peak ion chromatogram of oxycodone showing increased sensitivity in the absence of high voltage.

Conclusions

- ✓ Compounds ionise in the absence of high voltage – ∴ not electrospray
- ✓ Addition of ammonium acetate does not aid ionisation – ∴ not thermospray
- ✓ Turning off the electrospray high voltage can improve LOD e.g. oxycodone, reserpine data
- ✓ Suggests ions are formed in solution or during the supersonic jet expansion of carbon dioxide
- ✓ Acetonitrile as makeup or as modifier does not assist in ionisation unlike MeOH – ∴ supporting CRM?
- ✓ If sensitivity is an issue consider turning off the ESI high voltage

References

- [1] M. Garzotti, M. Hamdan, *J. Chromatogr. B*, 770 (2002) 53–61
- [2] R. Cole, *J. Mass Spectrom.*, 35 (2000) 763–772
- [3] A. Hirabayashi et al., *Anal. Chem.*, 67 (1995) 2878–2882
- [4] T. Arinobu et al., *Chromatographia*, 57 (2003) 301–307
- [5] Z. Takacs et al., *Anal. Chem.*, 75 (2003) 1514–1523

Acknowledgements

