

Performance of the API ion sources, ESI, APCI, and SSI under different eluent conditions for opiate analysis

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Since the introduction of atmospheric-pressure ionisation (API) devices the application of LC-MS has enlarged significantly in different areas and this trend will undoubtedly keep expanding in the future. Atmospheric-pressure chemical ionisation (APCI) and electrospray ionisation (ESI) are the most commonly used while sonic spray ionisation (SSI) is a more novel technique up to now applied only in a limited number of occasions. Although all three generate ions at atmospheric pressure each is characterised by a specific ionisation mechanism. One of the most critical issues is their behaviour under different eluent compositions.

We tested the performance of ESI, APCI, and SSI under different eluent conditions using morphine as model compound. Optimisation of the settings of the ion source and the ion trap based mass analyser (M-8000, Merck KGaA Darmstadt) as well as evaluation of the influence of the eluent composition were performed by flow injection analysis. By installing the syringe pump and the LC gradient pump in parallel, the effect of an increasing amount of the evaluated solvent on the ionisation efficiency of morphine could be clearly visualised. We investigated the influence of organic solvents (methanol and acetonitrile), volatile acids (formic and acetic acid), and buffers systems (ammonium formate and -acetate, with or/and without pH adjustment) for all three interfaces. For ESI the presence of organic solvents gradually increased the ionisation efficiency of morphine, while volatile acids or buffers gave a significant signal suppression. An almost identical behaviour was observed for SSI with the

exception of the effect of methanol. Not only did this not enhance the ionisation, at more than 80% methanol present a decrease was seen. APCI showed a completely different performance. Acetonitrile slightly suppressed the ionisation during the gradient run while methanol enlarged it. The presence of acids and buffers at the original pH of 6.8-7.2 doubled the intensity, and adjusting the pH to 4-4.5 increased the ionisation efficiency with almost 200%. An explanation for these phenomena might be found in the ionisation mechanism which in case of ESI and SSI starts mainly as a liquid-phase process and for APCI commences in the gas-phase.

This work was performed in cooperation with Merck KGaA Darmstadt and supported by Merck Eurolab Belgium.