

Electrospray Mass Spectrometry: A View From Inside The Capillary

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In this two-part seminar, a novel electrochemical probe will be described that has been designed, built, and used to characterize the distribution in solution potential within the electrospray (ES) device. The measurement system consists of three electrodes – a counter electrode held at highly negative potential that serves as the cathode, and two anodes consisting of a disk-shaped, mobile, internal (working) electrode, and the internal surface of the surrounding ES capillary (auxiliary electrode, held at ground potential). One-dimensional Differential Electrospray Emitter Potential (DEEP) maps detailing solution potential gradients within the electrospray emitter and in the region of the Taylor cone will be presented. Elucidation of the electrochemical details of the electrospray process can lead to mass spectrometric signal enhancement of certain species present in the spraying liquid, and also allow the detection of molecules that are usually not observable due to their low ionization efficiencies. The second part of the seminar will focus on the influence of the diameter of the spray tip employed for nano-electrospray mass spectrometry (nano-ES-MS) upon mass spectral charge state distributions of peptides and proteins. Under a variety of experimental conditions, the charge state distributions consistently shifted toward higher values as the tip orifice diameter decreased. This finding indicates that the use of narrow diameter capillaries can promote the formation of higher charge state ions that are more reactive precursors in tandem mass spectrometry experiments.