Spray Ionization Interfaces for Surface Sampling with Mass Spectrometry

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Novel Aspect: Full scan and automated product ion mass spectra acquired by sampling TLC plates with surface sampling ES or APCI

Introduction:
The ability to sample materials from surfaces with spray ionization interfaces is an area of increasing research (Van Berkel, et al., Anal. Chem. 74, 6216, 2002;Wachs and Henion, 73, 32, 2001). We report progress in the hyphenation of TLC and MS using surface sampling ES and APCI probes. Recent advances in our system include the use of an ion trap mass pectrometer, which allows aquisition of full scan or automated product ion mass spectral aquistion, while surface scanning (in either positive and negative ion modes), and the use of APCI in addition to ES. Improvements in the experimental set-up also include observation and TLC plate handling capabilities. Each of these advancements will be reported on in this presentation.

Methods:
TLC of ES or APCI favorable dye, anti-biotic and steroid compounds was performed on reverse phase C8 and C18 stationary phase TLC plates. TLC plates were mounted in the Y plane relative to the ion inlet of the mass spectrometer using an in-house designed TLC plate holder. The plates were positioned relative to the surface sampling interface using a PC controlled x, y, z microscope stage. Surface sampling operations were monitored using a 60X CCTV camera connected directly to the PC. ES and APCI mass spectrometry was performed in positive and negative ion modes on a Thermo Finnigan DecaXP plus ion trap.

Preliminary results:
ES or APCI surface sampling was applied to the analysis of TLC separated synthetic dye and anti-biotic compounds. TLC/MS data was acquired in an automated lane scanning mode of operation. Both positive and negative ion full scan mass spectra were taken while the TLC plates were scanned relative to the surface sampling probe. The advantages of using the two different ionization modes was made apparent by the difference in response of the target analytes when using the different ion sources. For example, sulfonic acid dyes were only identified using negative ion mode ES, whereas cationic species like rhodamine where observed only in positive ion mode ES. The chromatographic data both from visual inspection and TLC/MS analysis of the TLC plates adds significant strength to the function of TLC as a routine laboratory tool. TLC/MS allowed the identification of an degradation product of the reference dye mix which would have been un-assigned using conventional UV/Vis methods. Also the optical properties of the aging product were such that it was unidentified in a parallel visible wavelength densitometry analysis. Improvements in the surface sampling experimental set-up and the increased efficiency of the ion trap enabled the exploitation of the more complex scan functions of the mass spectrometer. The data dependent product ion scan function of the DecaXP Plus was used to perform automated TLC/MS/MS while scanning the surface of a TLC plate with the surface sampling probe. The MS/MS allowed structural assignment to the aging product in the dye mix data.

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