K24 The Application of CE- and CEC-TOF/MS to the Analysis of Non-Traditional Drugs Used to Facilitate Sexual Assaults

Jennifer Greaux, BS, and Bruce R. McCord, PhD, Florida International University, Department of Chemistry, 11200 Southwest 8th Street, Miami, FL 33199*

After attending this presentation, attendees will become aware of a wide range of "non-traditional" drugs which have the potential to be used to facilitate sexual assaults as well as newer techniques for analyzing these drugs.

This presentation will impact the forensic science community by detailing the analysis of various drug mixtures to show that CE and CEC are both efficient and reliable techniques for the detection of drugs in sexual assault samples. It is hopeful that the techniques can then be used to aid authorities in prosecuting criminals accused of sexual assault in a quick but efficient manner.

The overall purpose of this project is to develop and optimize methods for the analysis of drugs which may be found in blood and urine specimens from sexual assault cases. Capillary electrophoresis coupled to electrospray ionization time-of-flight mass spectrometry (ESI-TOF- MS) permits the rapid separation and identification of these drugs. In addition, CE provides high efficiency due to its plug-like flow, which is valuable when separating mixtures. The use of capillary electrochromatography (CEC) coupled to time of flight mass spectrometry was also investigated. Because CEC is a hybrid technique of CE and HPLC, it offers both high efficiency and stationary phase selectivity. This is important when separating drugs with similar physical and chemical properties.

The first part of this project involved an optimization of injection parameters for the CE system. The drugs studied belonged to the following classes: anticholinergic (scopolamine), anticonvulsant (valproic acid), antidepressants (citalopram, doxepin, fluoextine, imipramine, paroxetine, sertraline, desipramine, nortriptyline), antihistamines (diphenhydramine, doxylamine, brompheniramine), antihypertensive (clonidine), cough suppressants (dextromethorphan), and muscle relaxants (carisoprodol, cyclobenzaprine). Mixtures of different DFSA candidate drugs and their metabolites in their salt form were prepared via a simple three step process: addition of 1% HCl in methanol, evaporation to dryness, and reconstitution of sample in water (Hudson). This provided higher sensitivities when compared to previous methods where mixtures were prepared in buffer and deionized water. In addition, a water plug was added prior to sample injection to help preconcentrate the sample via an in-line stacking process. Buffer systems examined for these analyses included phosphate and more volatile buffers, such ammonium phosphate, ammonium bicarbonate and ammonium acetate. Controlled studies were performed to determine their effect on MS signal intensity. The pH and concentrations of the buffers as well as the run voltage were adjusted to optimize CE separations. The mixtures were then separated by CE-MS on a fused silica capillary (50 µm internal diameter, 84.5 cm total length). Run times provided by the system were under 15 minutes, with UV detection possible in the first 5 minutes of the analysis. There appeared to be some overlap between peaks; however, the drugs were still able to be identified by the mass spectrometer based on their mass-to-charge ratio.

In the second part of this project, monolithic capillary electrochromatographic (CEC) stationary phases were developed to improve the selectivity and efficiency of the analysis of this group of compounds. These stationary phases were prepared in-situ via polymerization of various monomers in the presence of porogenic materials, creating stationary phases with high surface areas and good porosity. These properties also permit drug preconcentration prior to analysis. Stationary phases were tailored to provide specificity by changing the type of retentive monomers and porogenic solvent used during the polymerization process.

The analysis of various drug mixtures will be detailed to show that CE and CEC are both efficient and reliable techniques for the detection of drugs in sexual assault samples. It is hopeful that the techniques can then be used to aid authorities in prosecuting criminals accused of sexual assault in a quick but efficient manner.

Capillary Electrophoresis, Mass Spectrometry, DFSA

 ** Presenting Author*