A5 Identification of Alkaloids and Cutting Agents in Illicit Brazilian Cocaine Using Liquid Chromatography-Mass Spectrometry

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After attending this presentation, attendees will be briefed on a new methodology to analyze cocaine alkaloids and adulterants using liquid chromatography-mass spectrometry (LC/MS). Also, attendees will understand what compounds can be found in refined illicit cocaine seized in Brazil and discuss the experimental results with the authors.

This presentation will impact the forensic science community by serving as an appealing alternative to the traditional methods used in the analysis of cocaine alkaloids by GC/MS or GC/FID both requiring prior derivatization with MSTFA.

Drug impurity profiling can generate important information for drug law enforcement authorities. In fact, chemical correlation between samples can be established, and material from different seizures can be classified into groups of related samples and determined if different seizures were derived from the same source. Consequently, specific links between different suppliers and users can be structured, drug distribution routes and networks can be built up, and the geographic origin of drug samples may be identified.

Since 2007 Brazilian Federal Police has been working on its own cocaine impurity profiling program ("Perfil Químico de Drogas" also known as the "PeQui" Project). An alternative methodology to analyze cocaine alkaloids that can be reliable, faster and free of derivatization agents, which are expensive and toxic, were suggested in the establishment of the Brazilian Signature Program.

A LC/MS method is proposed for simultaneous identification and quantification of some cocaine alkaloids: ecgonine, methylecgonine, tropacocaine, benzoylecgonine, norcocaine, N-formylcocaine, trimethoxycocaine; and typical cutting compounds: benzocaine, phenacetin, caffeine, lidocaine, levamisole, hidroxyzine diltiazem. Samples of illicit hydrochloride cocaine and cocaine base from Brazilian

Federal Police apprehensions, in the period between 2009 and 2010, were analyzed by this methodology.

LC/MS analysis was performed on a time-of-flight (TOF) mass spectrometer with electrospray ionization (ESI) in positive ion mode, using full scan data. Compound identification is based on accurate mass, isotope pattern, and retention time information. Protonated molecules $(M+H)^+$ were the ions selected in the quantification of all analytes. The HPLC conditions tested were two different reversed-phase C18 columns. The method was optimized using a gradient of formic acid/ammonium formate in water and formic acid in acetonitrile.

The analysis of the same compounds were also tested on a LC/MS/MS system based on UHPLC and triple quadrupole (QQQ) mass spectrometer with electrospray ionization (ESI) in positive ion mode, using MRM (multiple reaction monitoring) mode, monitoring two transitions to each compound. The preliminary results obtained on ESI- QQQ experiments were comparable with ESI-TOF results and demonstrate that MRM experiments are a promising analytical scheme for identification and quantification of cocaine alkaloids and adulterants.

Tandem mass spectrometry (MS/MS) screening techniques using MRM monitoring are able to detect only the target compounds previously defined in the method, while TOF can look for untargeted compounds not originally sought, from accurate mass full scan data without rerunning the samples. For instance, it is possible to detect new adulterants in cocaine samples and to reprocess the original data with screening software/database commercially available in modern mass spectrometry equipments.

The methodology based on LC/MS analysis of refined illicit cocaine samples is a novel and reliable approach and it can complement existing gas chromatographic methods for cocaine impurity signature programs.

Cocaine, LC/MS, Profiling

 ** Presenting Author*