K2 Signature Analysis of 25 Illicit Cocaine Samples and a Comparison to Analysis by AccuTOF™ DART™

Jeri D. Ropero-Miller, PhD, Peter R. Stout, PhD, Edward J. Minden Jr., BS, and Nichole D. Bynum, MS, RTI International, Center for Forensic Sciences, 3040 Cornwallis Road, Building 3, Research Triangle Park, NC 27709; John F. Casale, BS, Drug Enforcement Administration, Special Testing Laboratory, 22624 Dulles Summit Court, Dulles, VA 20166; Insook Kim, PhD, Jennifer Runkle, BS, Marilyn Past, PhD, and Buddha D. Paul, PhD, Armed Forces Institute of Pathology, 1413 Research Boulevard, Building 102, Rockville, MD 20850*

After attending this presentation, attendees will gain an enhanced understanding of multiple techniques for characterization of illicit cocaine and their ability to assess purity, level of performance, and their ability to determine specific compounds of interest.

This presentation will impact the forensic science community by providing a comparison of established quantitative, chromatographic method to a novel qualitative time-of flight mass spectrometric method to determine the purity of illicit cocaine and its relative abundance of signature compounds.

Introduction: Characterization of 25 illicit cocaine samples was undertaken in support of a research project funded in part by the National Institute of Justice (NIJ Award # 2006-DN-BX-K019) examining the ratios of cocaine-related compounds in hair samples contaminated with cocaine. Various coca-related compounds, isotope ratios and solvent determinations among other parameters are used to determine the manufacturing process and geographical origin of cocaine exhibits. Furthermore, this information is a useful tool to answer questions related to cocaine distribution and trafficking.

A novel application of direct analysis in real time (DART) sample introduction coupled with time-of-flight (TOF) mass spectrometry was evaluated for analyzing 25 samples of bulk powdered illicit cocaine hydrochloride salt seized by the Drug Enforcement Administration (DEA). The cocaine samples were analyzed by the DEA to determine their "signature" including their purity and the presence of specific compounds including products of manufacture, adulterants, and other cocaine analytes including oxidation products. The results of the analysis were then compared to data obtained by CFS to assess the AccuTOF-DART's level of performance.

Methods: Analysis was conducted in positive mode using AccuTOF- DART mass spectrometry. After analysis of the cocaine samples, each data set was examined for the presence of cocaine analytes (e.g., cocaine, benzoylecgonine, ecgonine ethyl ester, cocaethylene, norcocaine, anhydroecgonine methyl ester, truxillines, other ethyl esters) and a number of compounds typically found in illicit cocaine. These compounds include methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), ethyl acetate, n-propyl acetate, isopropyl acetate, mannitol, and petroleum ethers. Data obtained from both DEA signature analysis and AccuTOF-DART were compared to evaluate the level of performance of the AccuTOF-DART. Samples were also submitted to the Armed Forces Institute of Pathology (AFIP) for a limited GC-EI-MSD method as an additional confirmation of the norcocaine content.

Results: The AccuTOF-DART analysis of the cocaine samples resulted in the detection of the analytes anhydroecgonine methyl ester (AEME), tropacocaine, and trimethoxycocaine. Although AEME was easily detected, tropacocaine and trimethoxycocaine were detected intermittently, as were truxillines and MEK. In most samples, there was an ion present at 290.151 m/z, which is the M +H value of $C_{16}H_{19}NO_4$. This ion is consistent with both benzoylecgonine and its isomer norcocaine which have indistinguishable accurate masses. The table below shows the number of illicit cocaine samples in which the various components were detected by the three analytical processes (TOF-DART, DEA signature analysis, and AFIP GC-EI-MSD).

Using TOF-DART, further testing would be required under a different set of instrument parameters in order to distinguish the presence of norco- caine and/or benzoylecgonine. In these 25 cocaine samples, only trace quantities of cocaethylene were detected by DEA signature analysis.

Conclusions: This study has demonstrated the AccuTOF-DART's ability to analyze cocaine quickly and effectively. The TOF-DART is an adequate screening tool, but it does not currently have the level of perform- ance required for purity calculations. The AccuTOF-DART provided some, but not all of the signature compounds determined to be present in the samples analyzed by other established methods. Within these 25 cocaine samples, one cocaine sample had norcocaine present at approximately 8% when compared to the cocaine. However, because of the intermittent detec- tion of some of the analytes, variables such as sampling and instrument parameters need to be further investigated. Based on these samples, the DART-TOF would be a useful tool for the screening of samples and in some but not all circumstances may provide conclusive determination of chemical identity. These data will be used for future contamination studies in hair performed at RTI.

 ** Presenting Author*

Technique	AEME	BE	CE	NCOC	Trimethoxy-cocaine	Tropacocaine	Truxillines	Total Cinnamoyls
TOF-DART	22	25*	ND	25*	5	7	25	ND
DEA	ND	21	7	21	25	25	25	25
AFIP	23	NR	ND	7	NR	NR	NR	NR

* NCOC and BE indistinguishable by TOF-DART.

Cocaine, TOF-DART, Analysis

 ** Presenting Author*