B170 Analysis of Adulterated Phenethylamines Using Capillary Zone Electrophoresis

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After attending this presentation, attendees will be introduced to a simple methodology using capillary zone electrophoresis for the quantitation of several phenethylamines, followed by chiral determination. The attendees will also become familiar with some of the limitations associated with this methodology.

This presentation will impact the forensic community and/or humanity by describing a simple and rapid technique utilized to quantitate several phenethylamines in the presence of common adulterants/by-products found in routine illicit samples. Furthermore, with the simple addition of a chiral selector, the chirality of the phenethylamine can be determined.

A simple, rapid, and robust method for the quantitation of phenethylamine analogs using capillary zone electrophoresis (CZE) was developed. Among the more well known analogs in this family are amphetamine, methamphetamine, and 3, 4- methylenedioxymethamphetamine. These compounds are most often produced in clandestine laboratories by a variety of synthetic methods using easily obtainable precursors. Illicit samples often consist of complex mixtures multi-drug, precursors and by-products. Capillary electrophoresis provides an attractive alternative method to traditional high pressure liquid chromatography (HPLC) and gas chromatography (GC) methods that permits direct analysis of aqueous samples without the need for extraction or the use of organic solvents. The use of aqueous buffers reduces analysis cost and allows for simple disposal of waste solutions. Because neutral compounds migrate at the rate comparable to the electroosmotic flow (EOF), while the negatively charged acidic compounds migrate at a rate slower than the EOF, these species are not detected by CZE. Therefore, adulterants such as caffeine or acetaminophen do not interfere with quantitation by CZE. For example, when quantitating a tablet containing 30 mg of pseudoephedrine HCl with 500 mg of acetaminophen, because the latter migrates at a slow rate, it is not detected in the time range of analysis and is flushed from the capillary at the end of analysis. On the contrary, the same analysis by HPLC or GC results in column overload that negatively impacts the chromatography and quantitation. Moreover, capillary zone electrophoresis offers the advantages of being capable of analyzing samples over a broad pH range, avoiding potential problems with thermally labile substances, and is also relatively inexpensive.

The current method utilized is capable of resolving complex mixtures commonly encountered in routine illicit drug analyses. The method described here uses a 34 cm x 50 µm uncoated capillary, 100 mM lithium phosphate buffer at pH 2.3, with an applied voltage of 14.5 kV, and with thiamine HCl as the internal standard. The system was validated by demonstrating that each of the analytes' responses was reproducible and linear within a broad range of concentrations, and recovery values were accurate. Various capillary lengths were used to determine the selectivity of target compounds in the presence of common adulterants/by-products found in routine illicit samples.

The determination of the enantiomeric form is required in some cases for Federal sentencing guidelines as well as for intelligence purposes. Hence, a method for chiral separation by CZE was utilized. Figure 1 shows the chiral separation of amphetamine, methamphetamine, MDA, MDMA and MDEA on a 34 cm capillary using the same instrumental parameters mentioned above, but adding 20 mM 2-hydroxpropyl-beta-cyclodextrin to the lithium phosphate buffer as the chiral selector. All enantiomers for the standards were resolved. Hence, when the same methodology was utilized on actual samples virtually all methamphetamine samples analyzed were concluded to be the optically pure d form. In one case originating from Saipan, various proportions of l- and d-methamphetamine were present, which suggested that differing amounts of optically pure products having opposite isomers were mixed post synthetically.

The current study demonstrates that CZE performed on 34 cm uncoated capillaries using 100 mM lithium phosphate buffer is an effective technique for the quantitation of phenethylamine analogs. Quantitative results are all accurate, reproducible, and precise. The use of thiamine HCl as the internal standard was convenient, did not interfere with any known controlled substance or adulterant, and was commercially available at low cost. Chiral separation is conveniently accomplished on the same system with the addition of 2-hydroxypropyl- beta - cyclodextrin to the buffer. This simple methodology enables a laboratory to easily prepare all solvents and buffers in-house and to analyze a broad range of small molecules. This methodology has been used to quantitate hundreds of seized exhibits over the last three years, many of which were subsequently verified by other chromatographic techniques.

 ** Presenting Author*

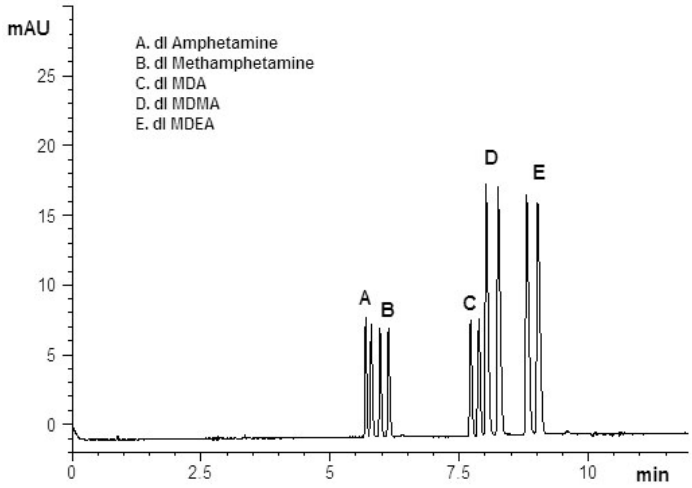

Figure 1: Separation of five phenethylamine racemic pairs on a 34 cm capillary. Background electrolyte consists of 100 mM lithium phosphate buffer containing 20 mM 2-hydroxypropyl-â-cyclodextrin as the chiral selector.

Forensic Science, Capillary Electrophoresis, Phenethylamine

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