B37 Analytical Data for Ortho-, Meta-, and Para-Chlorophenyl-Piperazines (CPP)

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After attending this presentation, attendees will be briefed of the problems associated with identifying the ortho, meta and para- chlorophenyl-piperazine (CPP) isomers.

This presentation will impact the forensic community by demonstrating that a conclusive identification of the meta- and para-CPP isomers is not possible using gas chromatography and/or mass spectrometry. The purpose of this study was to look for alternative ways to make conclusive identifications of CPP isomers using HPLC, GC, GC/MS, GC/IRD, and FTIR.

Background: A new drug has arrived on the drug scene, 1-(3- chlorophenyl)-piperazine, commonly known as meta-CPP or mCPP. In the United States, mCPP tablets have been identified in several mid-western states, including Texas, Iowa, and Illinois. In 2006, three suspected ecstasy tablets were seized in Stillwater, Oklahoma and submitted for identification. A preliminary identification of mCPP was made. After referring to article in Microgram, which stated that a forensic lab had originally misidentified mCPP as pCPP, it was decided further analysis of the Oklahoma tablet was necessary.

Methods: Initially, an Agilent 6890 GC was used for screening. The compounds were analyzed on two different column types, DB-1 and HP-50, with the same instrument conditions. The DB-1 column retention times for the different compounds were: ortho-CPP – 4.08, meta-CPP – 4.49, para-CPP – 4.52, mixture – 4.08, 4.50 and 4.52. The 4.50 and 4.52 peaks were not baseline separated. The HP-50 column retention times were: ortho-CPP – 4.30, meta-CPP – 4.80, and para-CPP 4.80. The mixture had only two peaks at 4.31 and 4.80.

Subsequently, an Agilent 5973 GC/MS equipped with a DB-1 GC column illustrated that the mass spectra of meta-CPP and para-CPP are identical. The ortho-CPP mass spectrum has additional ion peaks at 132 and 161. The combination of ion peaks and earlier retention time allowed for differentiation of ortho-CPP from meta- and para-CPP.

Upon completion of these experiments, it was determined that the GC retention times and mass spectra of the meta and para isomers were almost identical. A conclusive identification of either compound was not possible using gas chromatography and/or mass spectrometry.

The third type of analysis performed was GC/IRD utilizing an Agilent 6890 GC attached to a Digilab IRD II. A Rtx-1 GC column was used for the analysis. When comparing the three individual isomers, there are small, but distinguishable, differences in first peak grouping located between 3200 cm^{-1} and 2600 cm^{-1}. The principle peaks with the most differences are in the lower wavenumbers (1600 to 600 cm^{-1}). The three individual compounds are easily identified using GC/IRD. Modification of the GC method allowed sufficient separation of the isomer mixture to allow for identification.

The fourth type of analysis was FTIR spectrometry using ATR. The FTIR instrument used for analysis was a Magna-IR 550 Spectrometer Series II manufactured by Thermo Nicolet. The individual spectra for the different isomers were unambiguously different, with distinct characteristics throughout the spectrum (400 to 4000 cm^{-1}).

Lastly, HPLC analysis was performed on an Agilent 1100 LC equipped with a ZORBAX Eclipse-XDB C18 column. The mobile phase consisted of 5% acetonitrile and 95% of an aqueous mixture composed of 500 ml DI water, 0.35 gram decanesulfonic acid, 1 ml hexylamine and
2 ml phosphoric acid. The isomers were well resolved, allowing differentiation of the isomers. The retention times for ortho, meta and para isomers were 4.286, 7.901 and 9.210 minutes, respectively.

Conclusions: Conclusive identification can easily be made of the ortho-CPP isomer. It elutes at an earlier time on three different types of GC columns, and has different mass, IR and FTIR spectra when compared to the meta and para-CPP isomers.

The individual meta and para isomers cannot be distinguished using mass spectrometry, but are readily differentiated using IR and FTIR spectral data. If a mixture of these isomers is suspected, a technique such as GC-IRD could be used to separate and identify the components of that mixture. Alternatively, HPLC in combination with GC-MS can be utilized to determine which isomer(s) is present in such a mixture.

Drug Chemistry, mCPP, Chlorophenyl-Piperazine

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