B177 A Comparison of Gas Chromatography/Infrared Spectroscopy (GC/IR) and Gas Chromatography/ Mass Spectrometry (GC/MS) Methods for the Identification of Isomeric Synthetic Drugs

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Learning Overview: After attending this presentation, attendees will understand the role of gas chromatography/infrared spectroscopy (GC/IR) and gas chromatography/mass spectrometry (GC/MS) for the specific identification of individual regioisomeric substances from the synthetic cannabinoids, cathinones, and N-BOMe drug categories.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by focusing on vapor phase infrared spectroscopy as a confirmatory method of identification for regioisomeric synthetic drugs having equivalent mass based analytical signatures.

The overall goal of this study is to provide an analytical framework for the identification of isomeric forms of synthetic drugs. This presentation will focus on vapor phase infrared spectroscopy (GC/IR) as a confirmatory method of identification for regioisomeric synthetic drugs having equivalent mass based analytical signatures. Examples from several drug categories will be used to illustrate the advantages of GC/IR in the identification of regioisomeric synthetic drug substances, synthetic intermediates, and precursor chemicals.

The relentless development of new designer substances of synthetic origin creates challenges in forensic drug identification. The availability of a wide variety of precursor substances can yield numerous isomeric substances in several drug categories. Issues of regioisomerism are prominent in the cannabinoids, cathinone derivatives, N-methoxybenzyl-phenethylamines (N-BOMe) compounds as well as most other synthetic drug categories. Regioisomeric substances have the identical elemental composition, nominal and exact masses and in many cases yield regioisomeric fragment ions of equivalent elemental composition (equal mass).

The vapor phase infrared spectra are obtained at the elevated temperature of the GC transfer line under conditions equivalent to those used in GC/MS experiments. The higher temperature vapor phase removes many barriers of molecular conformational and rotational restraints yielding fewer individual peaks and broader bands. However, these vapor phase conditions yield spectra free from intermolecular interactions and matrix effects since the ultra-high-purity helium of the mobile phase is the only possible interacting species.

Regioisomeric forms of synthetic substances of equivalent elemental composition and yielding regioisomeric fragment ions of equal elemental composition present unique challenges in forensic drug identification using mass based analytical methods. The mass spectra for many regioisomeric substances are essentially identical and provide no unique ions for structural differentiation. Vibrational spectroscopy however measures small energy differences based on rotation/vibration amplitudes for individual molecular bonds. The interaction between neighboring bonds in regioisomeric substitution patterns yields unique and characteristic infrared absorption spectra.

The vapor phase infrared spectra for the twelve 1-*n*-pentyl-2-, 3-, 4-, 5-, 6- and 7-(1- and 2-naphthoyl)-indoles show the bridge position on the indole ring is a dominating influence over the observed carbonyl absorption frequency. Substitution on the pyrrole moiety of the indole ring yields the lowest C=O frequency values for position 2- and 3- giving a narrow range from 1656 to 1654 cm^{-1}. Carbonyl absorption frequencies are higher when the naphthoyl group is attached to the benzene portion of the indole ring yielding absorption values from 1674 to 1671 cm^{-1}. Furthermore, the inverse isomers (1-(1- and 2-naphthoyl)-3-n-pentylindole) show even higher carbonyl absorption in the 1705 cm^{-1} range.

Characteristic absorption bands for aromatic ethers in the 1500–1200 cm^{-1} range provide information concerning the position of the methylenedioxy ring and its relationship to the aminoketone side-chain in designer cathinone derivatives. The 2,3-methylenedioxy substitution pattern shows a characteristic absorption band consisting of a strong singlet centered in the 1450 cm^{-1} range. However, the 3,4-methylenedioxy substitution pattern shows a doublet absorption pattern in the same region. The equivalent region of the vapor phase infrared spectra provides a significant number of unique absorption bands characteristic for each individual dimethoxypyrovalerone regioisomer as well as the aromatic ring substituted precursor aldehydes and synthetic intermediate ketones.

This presentation will describe the use of GC-IR and GC/MS for the specific identification of individual regioisomeric substances from the synthetic cannabinoids, cathinones and N-BOMe drug categories. This work has established numerous chemical structure correlations with infrared spectral absorption patterns.

GC/IR, Synthetic Drugs, Isomer Identification