B199 Detection and Differentiation of Derivatized Controlled Substances by Gas Chromatography-Vacuum Ultraviolet (GC-VUV) Spectrophotometry

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Learning Overview: The goal of this presentation is to bring an understanding of GC-VUV spectrophotometry as applied to derivatized controlled substances.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by highlighting the capabilities of GC-VUV spectrophotometry to detect and differentiate derivatized controlled substances.

GC-VUV is a technique with the ability to differentiate isomers based on their spectra and is complimentary to Mass Spectrometry (MS). By probing sigma bonds and high energy pi bonds in the region of light from 120–430nm, every molecule aside from diatomic hydrogen can be detected. As interest in the technique grows, questions arise such as how various derivatization reactions change the spectrum of a molecule. To answer this question, the change in spectra by silylation and acylation of drugs, including methamphetamine, methcathinone, ephedrine, pseudoephedrine, fentanyl, and carfentanil, were analyzed by GC-VUV.

Derivatization is performed when working with analytes having low volatility, thermal instability, or when functional groups known to adversely affect the chromatographic performance of the analyte are present. By exchanging polar or active groups with more non-polar or inactive groups, increased volatility and improved chromatographic performance on polydimethylsiloxane columns can be obtained. Derivatization also improves the thermal stability of compounds such as methcathinone, which is known to degrade with time, temperature, and light exposure. When analyzed by GC/MS, derivatized compounds experience a shift in retention time and fragment ions with increased mass based upon the added functional group(s). Using GC-VUV, the retention time shift is maintained, but the difference is seen in absorptivity. Acylating reagents such as Trifluoroacetic Anhydride (TFAA) add a new pi-bond to the molecule that is detected in the VUV spectrum, alkylating and silylating reagents will adjust the sigma-bond regions. Vibronic coupling of the molecules will result in altered spectra based on distance of the functional groups to VUV absorptive groups within the molecule. Compounds with no active hydrogens, such as fentanyl and several of its analogs, require a different derivatization reagent, such as Pentafluorobenzyl-Hydroxylamine (PFBHA), an acylation reagent, to react with the ketone group.

Results indicate improved response in the pi-bond region of the spectra for acylation derivatization of most compounds. Improved response leads to increased peak area, which produces lower limits of detection and quantitation than for non-derivatized forms of the same drug. Peak shape in the form of asymmetry also improves for compounds with active functional groups (i.e., methamphetamine). Several de-identified “street” samples were analyzed to show “real world” performance.

It should be noted that VUV has difficulties differentiating small alkanes and should be considered as complimentary to GC/MS rather than as a replacement. Overall, GC-VUV continues to show promise for future use in forensic drug analyses as a technique complimentary to GC/MS.

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GC-VUV, Derivatization, VUV Detection

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