B66 Thermochemical Characterization of Cannabinoids by Porous Layer Open Tubular-Cryoadsorption (PLOT-Cryo) and Nuclear Magnetic Resonance (NMR)

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After attending this presentation, attendees will understand the importance of characterizing thermophysical properties (both vapor pressure and enthalpy of association) of two important cannabinoids, Cannabidiol (CBD) and Δ^9-Tetrahydrocannabinol (Δ^9-THC), for the development of useful, in-the-field vapor phase detection devices to aid law enforcement personnel in determining recent illicit drug use.

This presentation will impact the forensic science community by providing insight into the complexities surrounding the two most important questions that need to be addressed to develop an in-the-field vapor phase detection device to determine cannabinoid intoxication: (1) what is the correct "catch" material and how is it made selective for the compounds that will indicate intoxication; and, (2) what is the correct way to "release" these compounds for accurate analysis. This presentation will provide the chemical foundation necessary to begin to answer these non-trivial questions.

Decreased criminalization of cannabis has led to a surge in both medical and recreational use. Different plant cannabinoids impart either a therapeutic or psychoactive effects (e.g., CBD and Δ^9-THC, respectively). The physical and chemical properties of cannabinoids are difficult to investigate because cannabinoids are unstable in the presence of oxygen and heat. It is also difficult to detect recent use/abuse of cannabis with a chemical or biological test. While methods do exist to detect Δ^9-THC in the blood, urine, saliva, breath, and hair, these tests cannot indicate either recent use or intoxication/impairment.

In this study, the vapor pressure and enthalpies of association of Δ^9-THC and CBD were characterized by use of the ultra-sensitive, quantitative, trace headspace analysis technique, PLOT-cryo, and a 600MHz NMR spectrometer.[1-3] In the first experiment, PLOT-cryo was used to make thermodynamic measurements of the enthalpy of vaporization of select cannabinoids. The mass collected in the vapor phase is presented in the form of a Van't Hoff equation plot, which plots the concentration collected as a function of headspace collection temperature. A linear relationship of the recovered mass as a function of inverse collection temperature reveals the predictive capability of the methodology employed here.

In addition to PLOT-cryo techniques, NMR has been used to examine minute structural changes of Δ^9-THC and CBD in the presence of selected modifiers (such as Gas Chromatography (GC) stationary phases) and solvents. The ability to monitor intermolecular interactions of specific protons in biologically active molecules provides a more in-depth understanding of the thermodynamic and kinetic data associated with intermolecular interactions than is usually possible and is important in evaluating physiochemical properties and reactivity parameters. These parameters, such as association constants and enthalpies of association, have successfully been used to model thermodynamic and kinetic data. The resulting data were used to develop solvation models, which are used to guide research in more effective and rapid separation and detection methods and for the development of future field-ready detection devices.

Measurements on the vapor pressure and enthalpy of sublimation for pure Δ^9-THC and pure CBD will be presented as well as the enthalpies of associations of these compounds with different GC stationary phases. In

conclusion, these important thermochemical data will inform the most useful materials for catch and release of cannabinoids for in-the-field law enforcement detection device development.

Reference(s):

1. Lovestead T.M., Bruno T.J. Detection of poultry spoilage markers from headspace analysis with cryoadsorption on short alumina PLOT columns. *Food Chemistry*. 2010. 121(4): p. 1274-1282.
2. Lovestead T.M., Bruno T.J. Detecting gravesoil with cryoadsorption on short alumina PLOT columns. *Forensic Sci. Int.* 2011. 204: p. 156-161.
3. Lovestead T.M., Bruno T.J. Trace Headspace Sampling for Quantitative Analysis of Explosives with Cryoadsorption on Short Alumina PLOT Columns. *Analytical Chemistry*. 2010. 82(13): p. 5621-5627.

Cannabinoids, Drugs of Abuse, Headspace