Forensic Chemistry 5 (2017) 79–85

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.elsevier.com/locate/forc

Full length articles

Determination of cannabinoid vapor pressures to aid in vapor phase detection of intoxication ☆

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A R T I C L E I N F O

Article history:
Received 7 April 2017
Received in revised form 21 June 2017
Accepted 24 June 2017
Available online 27 June 2017

Keywords:
Cannabidiol (CBD)
Headspace (HS)
Porous layer open tubular-cryoadsorption (PLOT-cryo)
Δ^9-Tetrahydrocannabinol (THC)

A B S T R A C T

The quest for a reliable means to detect cannabis intoxication with a breathalyzer is ongoing. To design such a device, it is important to understand the fundamental thermodynamics of the compounds of interest. The vapor pressures of two important cannabinoids, cannabidiol (CBD) and Δ^9-tetrahydrocannabinol (Δ^9-THC), are presented, as well as the predicted normal boiling temperature (NBT) and the predicted critical constants (these predictions are dependent on the vapor pressure data). The critical constants are typically necessary to develop an equation of state (EOS). EOS-based models can provide estimations of thermophysical properties for compounds to aid in designing processes and devices. An ultra-sensitive, quantitative, trace dynamic headspace analysis sampling called porous layered open tubular-cryoadsorption (PLOT-cryo) was used to measure vapor pressures of these compounds. PLOT-cryo affords short experiment durations compared to more traditional techniques for vapor pressure determination (minutes versus days). Additionally, PLOT-cryo has the inherent ability to stabilize labile solutes because collection is done at reduced temperature. The measured vapor pressures are approximately 2 orders of magnitude lower than those measured for *n*-eicosane, which has a similar molecular mass. Thus, the difference in polarity of these molecules must be impacting the vapor pressure dramatically. The vapor pressure measurements are presented in the form of Clausius-Clapeyron (or van't Hoff) equation plots. The predicted vapor pressures that would be expected at near ambient conditions (25 °C) are also presented.

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1. Introduction

1.1. Cannabis

Cannabis is currently a Schedule 1 drug (illegal under federal law). In recent years, however, there has been a shift in some local or state policies towards the decriminalization of cannabis use. Decreased criminalization may lead to an increase in cannabis use and cannabis-related harm [1,2]. Potentially negative impacts include: a rise in intoxicated drivers and workers, an increase in cannabis use among adolescents, and negative health effects from chronic cannabis use [3–7]. Unlike alcohol consumption, which can be detected by monitoring the concentration of ethanol in the blood or breath, determination of cannabis intoxication is not as straightforward.

The cannabis plant contains over 500 compounds, including more than 100 plant cannabinoids that have been isolated and identified [8–10]. Some of these plant cannabinoids impart therapeutic or psychoactive affects, e.g., cannabidiol (CBD) and Δ^9-tetrahydrocannabinol (Δ^9-THC), respectively [11]. CBD is thought to effect pain sensation and mood but very little research substantiating these claims exist. Because of its psychoactive properties, Δ^9-THC is a molecule of great interest in the research and law enforcement communities. However, there are several aspects of the compound Δ^9-THC that make collecting and analyzing it in bodily fluids complex. For one, Δ^9-THC is rapidly metabolized in the body into both a psychoactive (the hydroxylated metabolite) and a non-psychoactive (the carboxylated metabolite) compound. Δ^9-THC is excreted in the urine as a glucuronic acid conjugate. Additionally, a small portion of Δ^9-THC is stored in adipose tissue

Abbreviations: CBD, cannabidiol; Δ^9-THC, Δ^9-tetrahydrocannabinol; EOS, equation of state; PLOT-cryo, porous layered open tubular cryoadsorption; GC–MS, gas chromatography–mass spectrometry; NBT, normal boiling temperature; FID, flame ionization detection; INChI, International Chemical Identifier; HS, headspace; TDE, ThermoDataEngine; TRC, Thermodynamic Research Center; SIM, selected ion monitoring; NIST, National Institute of Standards and Technology.

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http://dx.doi.org/10.1016/j.forc.2017.06.003
2468-1709/Published by Elsevier B.V.

and is released slowly over long time periods (hours, days, weeks). Δ^9-THC levels also depend on the mode of consumption (smoking versus eating) [12], when the user consumed [13], whether or not they are a chronic, an occasional, or a first time user [14], and of course, what body fluid is sampled [15]. In lieu of these complexities, some countries and states have set legal limits of Δ^9-THC concentrations in the blood, including zero tolerance laws to established impairment.

One major problem in addressing potential public health impacts of cannabis use is the lack of a noninvasive testing method to determine use, impairment, and intoxication. The most common methods for determining cannabis usage detect Δ^9-THC [6,7,12–21]. Devices that detect Δ^9-THC in the breath are currently being developed and have many advantages. Breath sampling is attractive because it is non-invasive, can be portable, and has been shown to indicate recent use within 0.5 h to 2 h [17]. Impairment, however, may last longer than can be observed by examining the exhaled vapors [17]. The ultimate goal for breath testing of Δ^9-THC is correlating Δ^9-THC concentrations in the breath to concentration in the blood, and thus, a potential determination of impairment, but the science for this correlation is still lacking.

To provide law enforcement personnel with the best breathalyzer for Δ^9-THC detection, a three-pronged research approach has been developed. First, fundamental data and models necessary for developing a Δ^9-THC breathalyzer will be provided; material properties for choosing the best materials for "catch" and "release" of Δ^9-THC will be investigated; and research into the chemical signature of breath that corresponds with cannabis intoxication will be conducted with "breatholomics" efforts. This approach is collaborative, and each prong is necessary for (and enables) the other efforts. For example, in order to develop the measurement science necessary to obtain fundamental data measurements and develop useful models, material properties will be characterized. Additionally, the chemical signature of the breath while intoxicated from cannabis usage will dictate which compounds require fundamental data measurements and where to focus modeling efforts. Collecting this chemical signature will require advances in material design and apparatus development. The focus of this work is fundamental data and models, specifically vapor pressure measurements.

1.2. Vapor pressure

Vapor pressure is the very first thing needed to begin a rudimentary equation of state (EOS). An EOS is necessary to provide an avenue for predicting thermophysical properties that are important for designing and engineering a specialized device such as a cannabis breathalyzer. Vapor pressure measurements can be used to predict the normal boiling temperature (NBT, temperature that the fluid boils at 1 atm), which can then be used to predict the critical constants (critical temperature, critical pressure and critical volume). The uncertainty of calculations from these models is of course dependent on the uncertainty of the input data; more data and lower uncertainty is always desirable. For cannabinoids, there are no available data, thus these will be the first available measurements for the field. Well-developed models like standard reference equations are based on hundreds of measurements, whereas the models developed here are a rudimentary beginning but are far better than "chemical intuition" for predicting the important thermophysical properties for device optimization.

Most commercial methods for measuring vapor pressure are designed to measure volatile or moderately volatile compounds. These methods typically require day to weeks to collect sample and can require large sample sizes. A previously developed technique employing porous layer open tubular-cryoadsorption (PLOT-cryo) technology made vapor pressure measurements of cannabinoids possible [22,23].

1.3. PLOT-cryoadsorption (PLOT-cryo)

PLOT-cryo is an ultra-sensitive, quantitative, trace dynamic headspace (HS) analysis technique that was used to determine the mass of sample collected from the vapor phase at a given HS collection temperature. This method is used for trace vapor analysis (of polar and non-polar solutes of moderate to low volatility) with high reproducibility and thermodynamic consistency. In PLOT-cryo, a sweep gas is carried through a fused silica tube into a sealed vial containing the sample, with the entire assembly located in an oven (Fig. 1). The HS vapors are then carried by the sweep gas and trapped on a PLOT capillary (Fig. 2) contained in a temperature-controlled cryostat. PLOT-cryo has the inherent ability to stabilize labile solutes because collection is done at reduced temperature. The PLOT capillary column is robust, reusable, inexpensive and has a large temperature operability for less volatile solutes. While alumina is used in this research, the sorbent phase can be tailored for the chemistry of interest. Analytes are eluted from the PLOT capillary using a suitable solvent or thermal desorption and a gas flow. The collected analytes are then analyzed by use of any instrumental technique, but typically gas chromatography-mass spectrometry (GC–MS).

Since the invention of PLOT-cryo, it has been applied to sampling spoiled poultry, gravesoil, pyrolysis products, explosives, and characterizing natural gas and fire debris [23–28]. For the gravesoil experiment, the method was modified to sample the HS air above gravesoil with a motorized pipetter and a PLOT capillary at ambient temperatures. This modified approach provided us with the first generation of an in-the-field trace vapor collection device. Since the gravesoil work, a much more capable in-the-field trace vapor collection device has been built, which utilizes the air compressor from a typical fire truck to provide the suction and temperature control [29,30]. No other energy inputs are necessary.

PLOT-cryo is an ideal technique for the determination of vapor pressures of cannabinoids. These compounds have very low vapor pressures and are unstable (reactive with oxygen). PLOT-cryo has the advantages of short sampling durations to minimize sample degradation allowing for highly accurate thermophysical properties data measurements on unstable (reactive) compounds. Additionally, PLOT-cryo has the inherent ability to stabilize labile solutes because collection is done at reduced temperature. Providing law enforcement with vapor pressure measurements on the main two important cannabinoids, Δ^9-THC and CBD, will help to develop correlations between cannabinoid concentration detected in the breath and cannabinoid concentrations in the blood. Ultimately, these data will help make a breathalyzer for determining driving und the influence of cannabis.

2. Experimental

2.1. Materials

The solvents used in this work were acetonitrile and methanol. They were obtained from a commercial supplier. GC analyses (30 m capillary column of 5%-phenyl-95%-dimethyl polysiloxane having a thickness of 0.25 μm, temperature program from 50 °C to 170 °C at a heating rate of 5 °C per minute) with flame ionization (FID) and MS detection revealed the purity to be greater than 99%. These solvents were used without further purification [31,32]. CBD and Δ^9-THC were also purchased from a commercial supplier. Δ^9-THC was reported by the supplier to have a purity of ≥98% and it was provided as a solution in acetonitrile. The CBD was reported to have a purity of ≥99% and it was provided as a crystalline solid. These reported purities were confirmed with GC–MS analyses before experimentation. Δ^9-THC was already in solution and thus was used as received, and CBD solutions were prepared with methanol. Purity checks were made on a 30 m capillary column of 5%-phenyl-95%-dimethyl polysiloxane having a thickness of 0.25 μm. The inlet temperature was 250 °C with an inlet pressure of 82.73 kPa (12 psi).

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