D27 Partitioning Relationships to Quantitate Organic Molecules in Air or Breath Samples

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Learning Overview: After attending this presentation, attendees will have learned about methods to quantitate organic molecules in air or breath samples, with a focus on sorbent-air and blood-air partition coefficients.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by describing methods to quantitate organic molecules in air or breath samples through the use of sorbent-air and blood-air partition coefficients. Quantitative partitioning information is crucial to numerous areas of forensic science; however, this presentation will focus on its application to the development of a cannabis breathalyzer device.

There is interest in terpenes and terpenoids produced by cannabis plants, which may be found in indoor environments such as greenhouses, isolated plant material, or exhaled breath. Cannabis plant material can be distinguished from similar plants by its major cannabinoids (Δ-9-tetrahydrocannabinol or cannabidiol); however, cannabinoids have low vapor pressures and are reactive; only small quantities will be captured at ambient temperatures.[1] Furthermore, highly odorous compounds that may be important for cannabis detection by humans or trained canines are not necessarily the compounds present in the highest concentration in the vapor phase.[2] Recent investigations indicated that three sesquiterpenes (α-santalene, valencene, and ß-bisabolene) are unique to cannabis, suggesting that terpenoids may be effective markers for cannabis for some applications.[3]

When air or breath equilibrates with a sorbent, sorbent-air partition coefficients describe the relative concentrations of molecules in the two phases and are required to quantify the original concentration of the analyte(s) of interest. For breath samples, blood-breath partition coefficients may enable blood concentration to be calculated from breath concentration. Passive air samplers are frequently employed to characterize exposure to hazardous chemicals in indoor and outdoor environments with adsorbent configurations designed to sample in the kinetic region (linear uptake) or the thermodynamic region (equilibrium).[4] Multiple adsorbents can be used, including activated charcoal and Polydimethylsiloxane (PDMS), which is deployed in the form of sheets or as sorbent-coated glass fibers. The exhaled breath of cigarette smokers and non-smokers was recently sampled with a capillary packed with sorbent-coated glass microfibers, resulting in high surface area that promoted sorbent-breath equilibration.[5]

This presentation describes research on PDMS, which can be coated onto glass fibers and has been used to concentrate analytes from both headspace and breath samples. Quantitative analyses require sorbent-air partition coefficients at both adsorption and desorption temperatures, which span at least 20°C to 200°C. Partition coefficients can be extrapolated within the linear range of the van't Hoff equation if sufficient experimental values are available; often they are not. This presentation will describe an empirical, temperature-explicit group contribution model to predict sorbent-air partition coefficients solely from molecular structure.[6] This study created the model with training compounds containing carbon, hydrogen, and oxygen, reflecting interest in phytochemicals such as terpenoids. Partition coefficients for the training compounds were calculated from Kovats retention indices and isothermal gas chromatography measurements at temperatures from 60°C to 200°C. This study compared model predictions to limited experimental values available at 25°C. The value of this modeling approach is its ability to incorporate all available data, which is advantageous for properties with limited experimental values at a single temperature. This presentation also discusses the important role of blood-air partition coefficients and investigates the use of static and dynamic headspace sampling methods for their measurement.

References:

1. Tara M. Lovestead and Thomas J. Bruno. Determination of Cannabinoid Vapor Pressures to Aid in Vapor Phase Detection of Intoxication. *Forensic Chemistry* 5 (2017) 79-85.
2. Somchai Rice and Jacek A. Koziel. The Relationship Between Concentration and Odor Activity Value Explains the Inconsistency in Making a Comprehensive Surrogate Scent Training Tool Representative of Illicit Drugs. *Forensic Science International* 257 (2015) 257-270.
3. Nancy Wiebelhaus, D'Nisha Hamblin, Natasha M. Kreitals, and Jose R. Almirall. Differentiation of Marijuana Headspace Volatiles from Other Plants and Hemp Products using Capillary Microextraction of Volatiles (CMV) Coupled to Gas-Chromatography-Mass Spectrometry (GC-MS). *Forensic Chemistry* 2 (2016) 1-8.
4. Aaron Lamplugh, Megan E. Harries, Feng Xiang, Janice Trinh, Arsineh Hecobian, Lupita D. Montoya. Occupational Exposure to Volatile Organic Compounds and Health Risks in Colorado Nail Salons. *Environmental Pollution* 249 (2019) 518-526.
5. D'Nisha Hamblin and Jose R. Almirall. Analysis of Exhaled Breath from Cigarette Smokers using CMV-GC/MS. *Forensic Chemistry* 4 (2017) 67-74.
6. Kavita M. Jeerage and Elijah N. Holland. Predicting Sorbent-Air Partition Coefficients for Terpenoids at Multiple Temperatures. *Industrial & Engineering Chemistry Research* 59 (2020) 16473-16482.

Breath Analysis, Partition Coefficient, Group Contribution Model