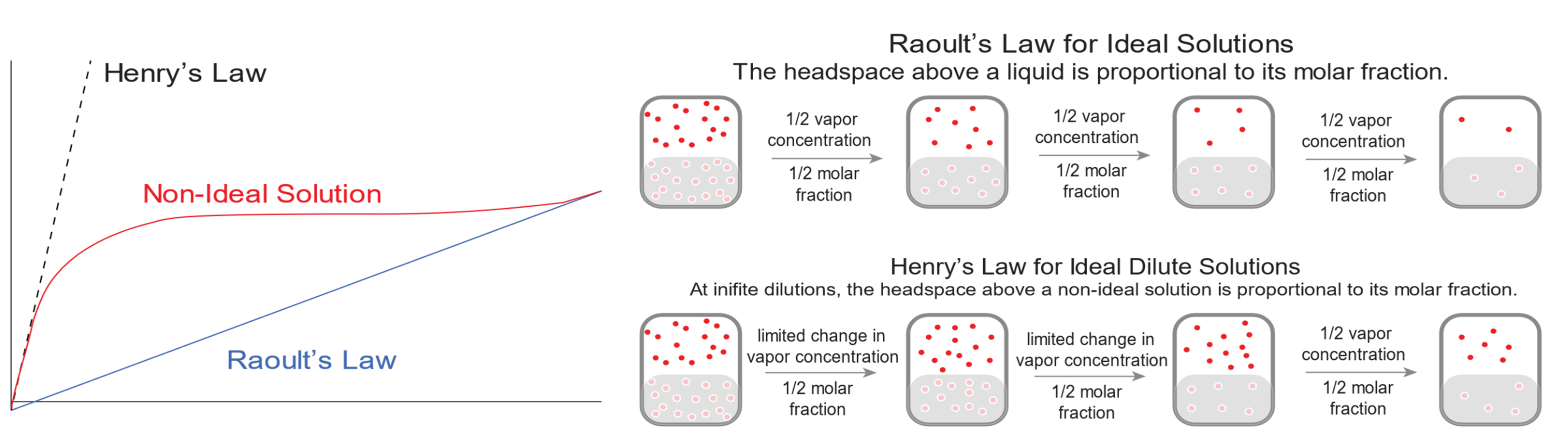
Measuring the Relationship Between Liquid and Vapor Phase Concentrations for Esters Diluted in Mineral Oil Using a Photoionization Detection-Based Approach

Vinaya Mapitiyage, Austin Pauley, and Adam Dewan
Department of Psychology and Program of Neuroscience, Florida State University

Introduction

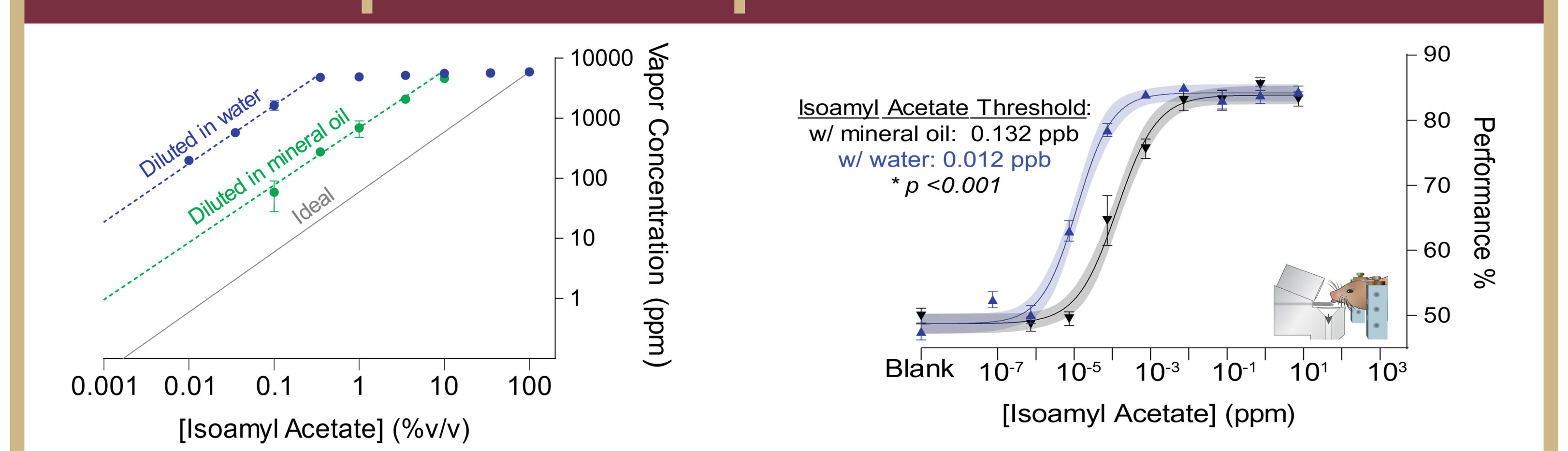
- Liquid dilutions are commonly used in olfactory research to adjust the vapor-phase concentrations of volatile odorants.
- **Goal:** assess the relationship between liquid and vapor-phase concentrations of ester acetates using our photoionization detector (PID) based method (Jennings et al., 2022).
- By subjecting a vapor sample to a strong ultraviolet light, PID ionizes the volatile molecules, producing a current that corresponds to the vapor concentration.
- **Significance:** The liquid-/vapor-phase equilibrium equations can be used by other researchers to obtain accurate vapor-phase ester concentrations

Odorants Rarely Follow the Laws of Proportionality



Odorants often deviate from the laws of proportionality resulting in higher-than-expected vapor-phase concentrations.

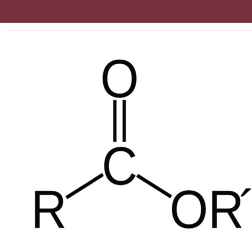
Vapor Phase Concentration is Dependent upon the Solvent



The vapor-phase concentration of an odorant can be influenced by its solvent and thus has the potential to confound the interpretation of functional experiments.

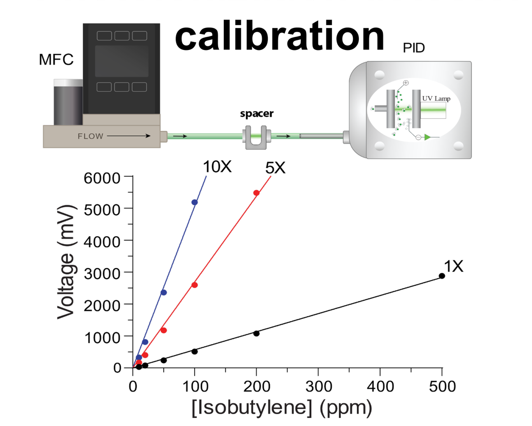
Ester Odorants

- Esters are classified as being a part of the ester functional group.
- Have pleasant, "fruit-like" odors.
- High volatility.
- Slightly soluble in water.



Methods

Photoionization detector calibration



PID is calibrated to isobutylene gas at different gain levels

Measuring the liquid- / vapor-Phase relationships

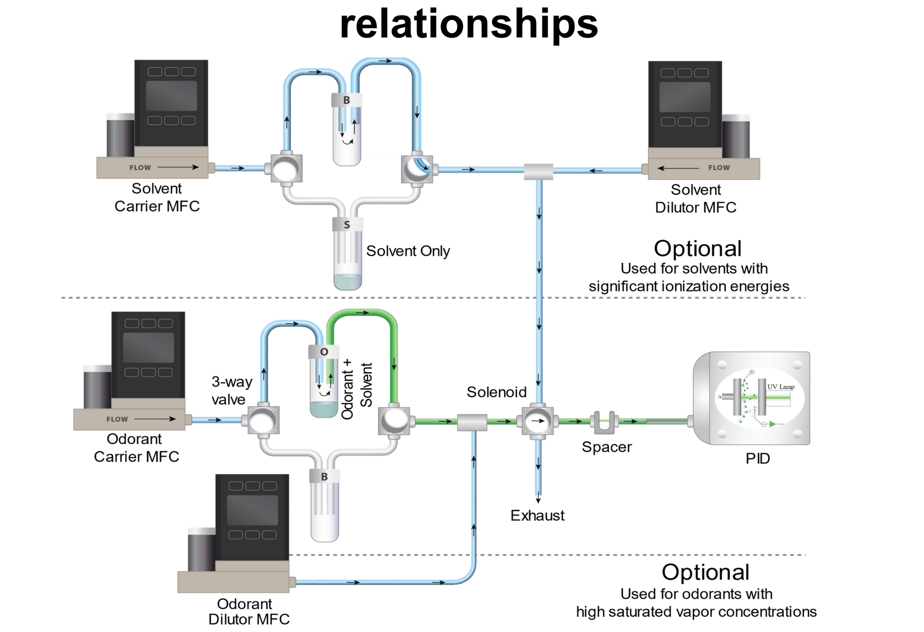
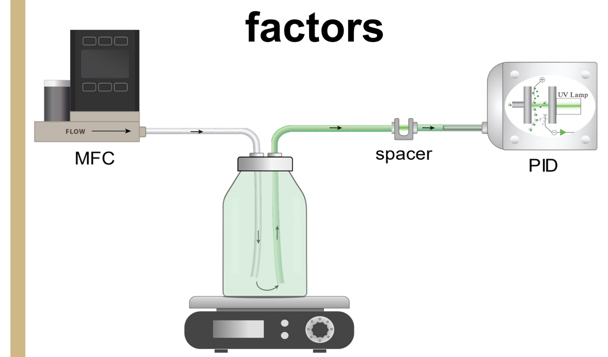


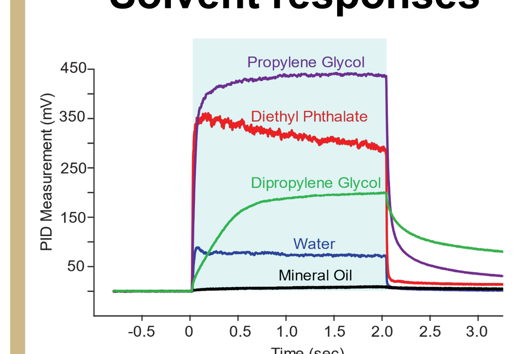
Diagram of PID-based method for measuring vapor-phase odorant concentrations in different solvents.

Measuring PID correction factors



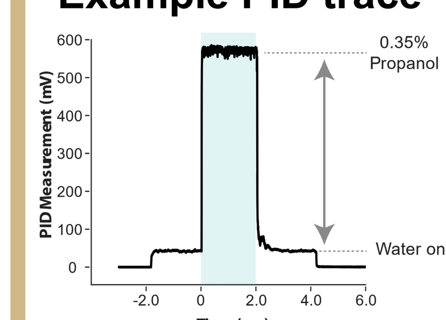
A sealed bottle with pure odorant was heated to its boiling point prior to PID measurement. The vapor concentration was divided by the resulting signal calibrated to isobutylene gas.

Solvent responses



Solvent responses can confound estimations of vapor-phase odorant concentrations.

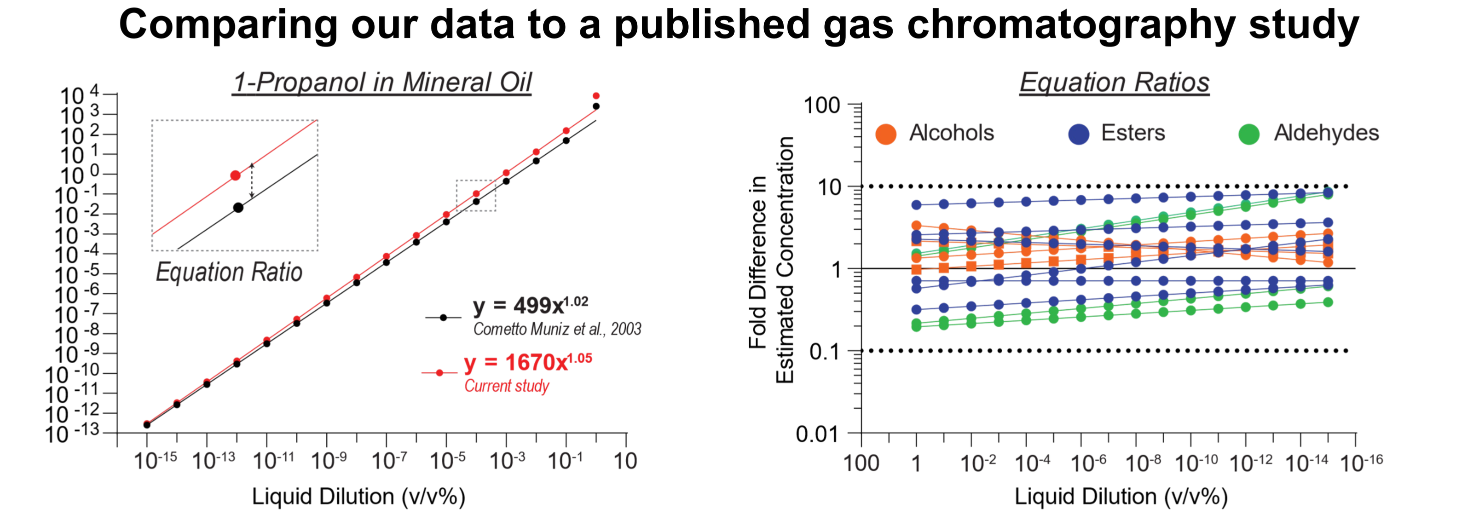
Example PID trace



The signal is calculated as the difference between the odorant in the solvent and the solvent alone.

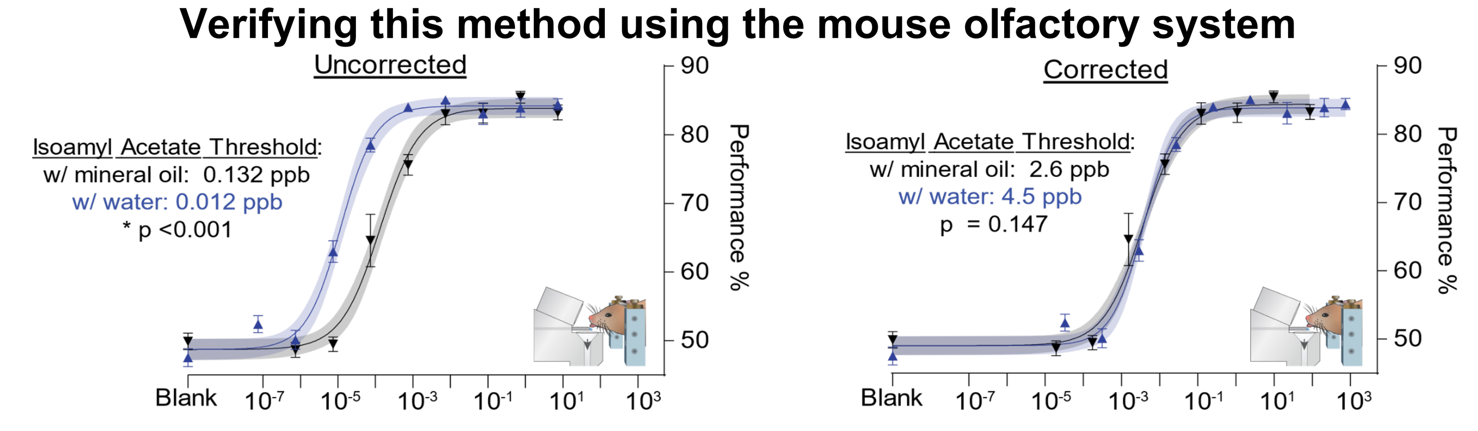
Validating the Method

Comparing our data to a published gas chromatography study



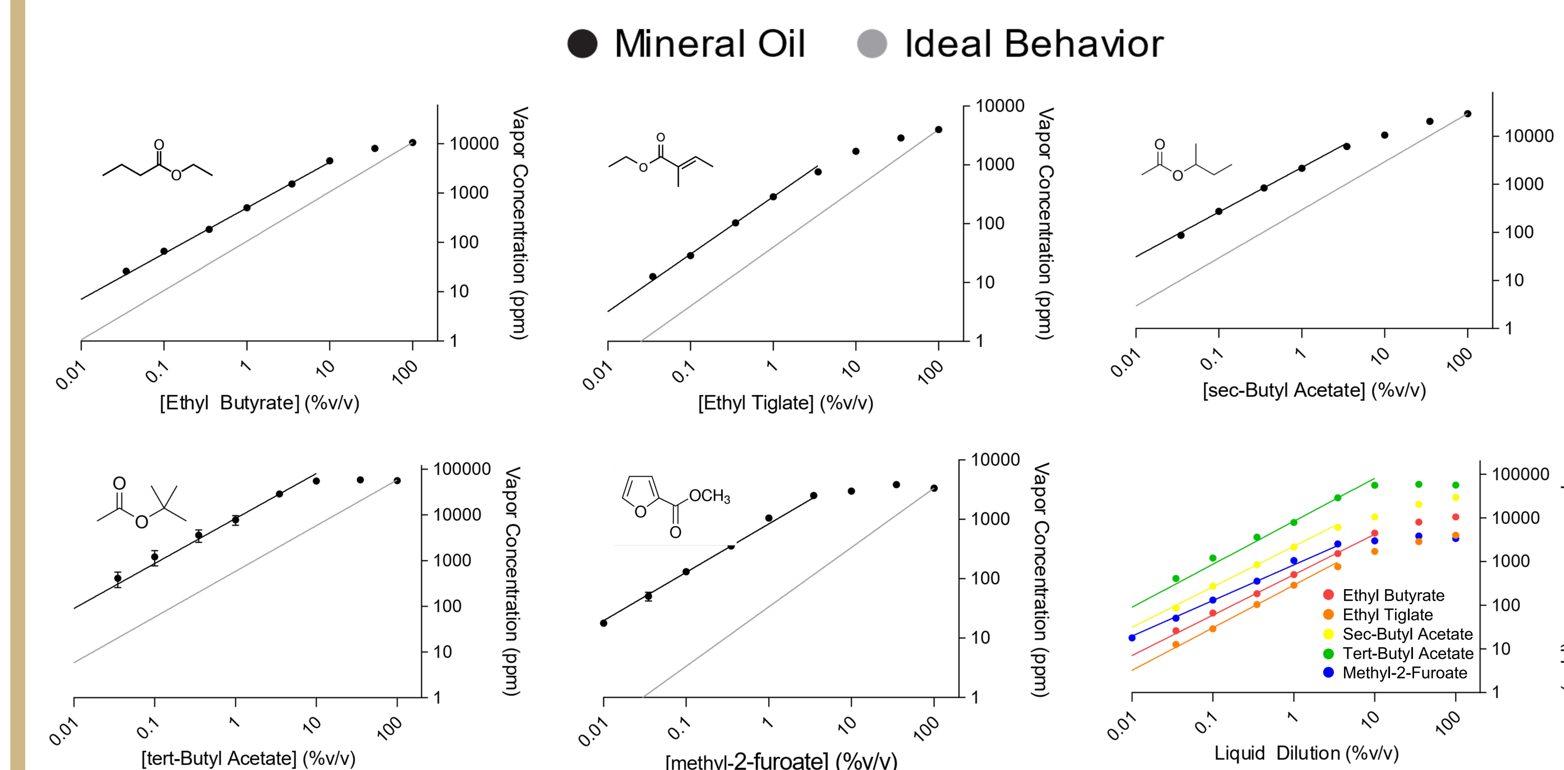
Our liquid-/vapor-phase equilibrium equations were reasonably similar to a previous study utilizing gas chromatography to estimate odorant concentration in mineral oil.

Verifying this method using the mouse olfactory system



Our liquid-/vapor-phase equilibrium equations successfully corrected for differences observed in animals tested with the same odorant in different solvents.

Results



Odorant	Correction Factor	Equilibrium Equations	
		Ideal	Mineral Oil
Methyl Butyrate	3.7	$y=232.9x^{1.00}$	
Ethyl Butyrate		$y=105.6x^{1.00}$	$y=499.8x^{0.93}$
Butyl Butyrate	1.4	$y=25.3x^{1.00}$	
Ethyl Tiglate	1.0	$y=39.9x^{1.00}$	$y=287.3x^{0.98}$
Ethyl Acetate	5.1	$y=1226.4x^{1.00}$	$y=87434.0x^{0.95}$
sec-Butyl Acetate	1.7	$y=293.4x^{1.00}$	$y=2234x^{0.93}$
tert-Butyl Acetate	4.1	$y=582.4x^{1.00}$	$y=8350x^{0.98}$
Methyl-2-Furoate		$y=33.6x^{1.00}$	$y=837.0x^{0.82}$

Summary

- Diluted esters exhibit near-ideal behavior in mineral oil.
- PID is reasonably accurate at measuring liquid- / vapor-phase equilibrium relationships in different solvents.
- Future experiments will analyze additional esters and utilize different solvents.
- The information will be added to a practical repository containing liquid/vapor-phase equilibrium equations for structurally diverse odorants in different solvents.

References

- Cometto-Muñiz, J.E., Cain, W.S., and Abraham, M.H. 2003. Quantification of chemical vapors in chemosensory research. Chem Senses. 28:467–477.
- Jennings, L., Williams, E., Caton, S., Avlas, M., & Dewan, A. (2022). Estimating the relationship between liquid- and vapor-phase odorant concentrations using a photoionization detector (PID)-based approach. *Chemical Senses*, *48*. https://doi.org/10.1093/chemse/bjac038