

PERFORMANCE OF THREE-WAVE MIXING ROTATIONAL SPECTROSCOPY FOR THE DETERMINATION OF ENANTIOMERIC EXCESS IN COMPLEX CHEMICAL MIXTURES

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The method of microwave three-wave mixing can be used to perform chiral analysis by molecular rotational spectroscopy.[1-3] We have developed pulse sequences that can be used to determine the enantiomeric excess (EE) of a component that is present in a complex mixture. To make an EE determination, the measurement needs both a chiral three-wave mixing measurement and a signal that is proportional to the total amount of the molecules. The measurement provides both the EE and the identity of the dominant enantiomer (Based on the phase). Furthermore, a sample of known EE must be available to generate a calibration curve. Validation measurements of the technique indicate that EE determinations with about 5% accuracy are possible using this technique. The major strength of three-wave mixing is its ability to perform EE measurements directly in complex mixtures. Unlike chiral tag rotational spectroscopy, three-wave mixing does not add to spectral congestion resulting from the formation of isomers with the chiral tag. The performance of the calibrated EE schemes presented previously at ISMS [4] and expanded in the previous talk will be presented for EE determinations of molecular components in essential oils. Primary validation comes from spiking a new chiral molecule with known EE into an essential oil. EE determinations of menthone and isomenthone in a series of commercial samples that have also been analyzed by the chiral tag method will be reported. These measurements show that both menthone and isomenthone are found in high enantiopurity in natural samples.

[1] D. Patterson, M. Schnell, and J.M Doyle, "Enantiomer-specific detection of chiral molecules via microwave spectroscopy", *Nature* 497, 475- 478 (2013). [2] D. Patterson and J.M. Doyle, "Sensitive Chiral Analysis via Microwave Three-Wave Mixing", *Phys. Rev. Lett.* 111, 023008 (2013). [3]J. Grabow, "Fourier Transform Microwave Spectroscopy: Handedness Caught by Rotational Coherence", *Angew. Chem. Int. Ed.* 52, 11698-11700 (2013). [4] M.S. Holdren, B. Pate, C. Embly, A. Wu, K.J. Mayer, J. Dittman, P. Buonicotti, G. Haghtalab, B. Mitchell, "Enantiomeric Excess Measurements using Microwave Three-Wave Mixing", Talk TC08, ISMS 73rd Meeting Archive, <https://dx.doi.org/10.15278/isms.2018.TC08>.