

CALIBRATING THE ENANTIOMERIC EXCESS OF CHIRAL TAGS TO IMPROVE MEASUREMENT ACCURACY USING A SIMPLIFIED 6-18 GHZ CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER

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The enantiomeric excess (EE) of a chiral sample can be determined from molecular clusters of the analyte and a chiral tag in a pulsed-jet expansion. The complexation converts analyte enantiomers into rotationally distinct diastereomer complexes. The EE is determined by comparing rotational transition intensities resulting from diastereomer complexes when a racemic tag is used and when an enantiopure tag is used. For a pair of diastereomer transitions, the connection between the normalized intensity ratio (R) and the analyte EE is: $(R-1)/(R+1) = (EE_{\text{analyte}})(EE_{\text{tag}})$. Therefore, accurately determining an analyte EE requires an accurate “enantiopure” tag EE. The EE calibration of three frequently used tags (3-butyne-2-ol, propylene oxide, and 2-(trifluoromethyl)oxirane) is described. For butynol, EE determinations are possible using homochiral and heterochiral dimers, known as “auto tagging.” Optimal sensitivity is achieved between 6-18 GHz due to the size of the dimers. A pulse generation system utilizing a frequency doubler with low harmonic generation is employed to improve spurious signal performance compared to schemes requiring an external reference clock. Several butynol dimer isomers are formed in the jet expansion, and EE determinations are equivalent regardless of the isomers used in the analysis. Determination of EE by auto tagging was validated by chiral GC. Also, a series of butynol samples with EE between 50 and 90 were prepared gravimetrically by mixing high enantiopurity butynol (EE = 98% by chiral GC and auto tag) with racemic butynol. Chiral tagging measured the EEs in this range with greater accuracy than chiral GC. The EEs of propylene oxide and 2-(trifluoromethyl)oxirane were determined by tagging with the calibrated butynol. Neither molecule reports an EE in their Certificate of Analysis, possibly because their high volatility precludes separation by chiral GC. To validate the EE determinations, both tags were used to measure the EE of an analyte and were found to be equivalent within measurement accuracy.