

All data taken at Pacific Northwest National Laboratory (PNNL)

Operators: Steven W. Sharpe, Timothy J. Johnson and Robert L. Sams : sw.sharpe@pnl.gov

Version 1.0, October, 01

Composite spectrum for CROTALD_5T

Effective burden of composite spectrum: 1 part-per-million-meter (ppm-meter) at 296 K

Equivalent concentration x path-length of composite spectrum: 2.886×10^{-6} grams/liter-meter

Sample Conditions-

- Chemical name and CAS number: trans-Crotonaldehyde, (E)-crotonaldehyde, (E)-2-butenal, trans-2-butenal, $\text{CH}_3\text{-CH=CH-COH}$: [123-79-9]
- Physical properties: fw=70.09 g/mole, fp=-76.5° C, bp=102° C
- Supplier and stated purity: Aldrich, 99%
- Sample class: II (PNNL scale). Extremely “sticky” with respect to O-rings and manifold.
- Temperature of sample: 5.05 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760 ± 5 Torr
- Individual samples at 7.7350, 1.06211, 2.0625, 3.1360, 0.56430, 4.0935 and 5.3800 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at -50 C to remove air. Sample placed over CaSO_4 to remove dissolved water.

Instrument Parameters-

- Bruker-66V FTIR, temperature controlled environment, evacuated optics bench
- Modified to include second aperture, between interferometer output and sample cell. This substantially reduces both “ghosting” and warm aperture effects.
- Spectral range: $6,500$ to 600 cm^{-1} (1.534 to 16.667 microns)
- Instrumental resolution based on maximum interferometer displacement is 0.112 cm^{-1}
- Spectral interval after 2X zero-filling interferogram and FFT: 0.06 cm^{-1}
- Interferogram zero-fill: 2X
- Apodization: Boxcar
- Phase correction: Mertz
- Beam splitter: Potassium bromide (KBr)
- IR source: Carbide glowbar (22 V)
- Scanner velocity: 60KHz (HeNe crossing frequency)
- Number of interferograms averaged per single channel spectra: 256
- Detector: Mid-band HgCdTe, photoconductive, 77K operation
- Folding limits: 15798 to 0 cm^{-1}

Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ($\alpha=0.90$, $\beta=500$)
- Composite spectrum created from 7 individual absorbance (base-10) spectra via classical least squares fit: Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values > 1.6 are given zero weight
- Calculated and estimated errors: Type A = 0.97%, Type B = 5%
- Frequency correction (already applied): $V(\text{corrected}) = V(\text{instrument}) * 0.999998 + 1.287 \times 10^{-4}$
- Axis units: X=wavenumbers (cm^{-1}), Y=Absorbance (base-10)
- Trace water vapor and carbon dioxide features removed via spectral subtraction. Some residual derivative structure remained due to possible pressure broadening effects.

- Baseline correction via 7th order polynomial subtraction