

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for ETNITRI\_50T

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

Equivalent concentration x path-length of composite spectrum:  $3.0906 \times 10^{-6}$  grams/liter-meter

Approximately 3% methyl nitrite observed in composite spectrum. Composite spectrum is rescaled to reflect 3%  $\text{CH}_3\text{NO}_2$  contamination.

### Sample Conditions-

- Chemical name and CAS number: Ethyl nitrite, nitrous acid ester, spirit of ether nitrite,  $\text{C}_2\text{H}_5\text{NO}_2$  : [109-95-5]
- Physical properties: fw=75.067 g/mole, fp=-35° C, bp=17.4° C
- Supplier and stated purity: Synthesized in house. See Frederick L. Rook, J. Chem. Eng. Data **27**, 72 (1982).
- Sample class: I (PNNL scale).
- Temperature of sample:  $50.05 \pm 0.02$  C
- Diluent: Sample back filled with ultra high purity nitrogen to  $760 \pm 5$  Torr
- Individual samples at 1.01464, 31.39, 16.39, 8.2029, 2.1957 and 4.1192 Torr. Path length = 19.94 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at 77 K to remove air.

### 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  $525 \text{ cm}^{-1}$  (1.534 to 19.048 microns)
- Instrumental resolution based on maximum interferometer displacement is  $0.112 \text{ cm}^{-1}$
- Spectral interval after 2X zero-filling interferogram and FFT:  $0.06 \text{ cm}^{-1}$
- 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  $0 \text{ cm}^{-1}$

### Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ( $\alpha=0.85$ ,  $\beta=530$ )
- Composite spectrum created from 6 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 = 3%
- Frequency correction (already applied):  $V(\text{corrected}) = V(\text{instrument}) * 0.99999896 + 8.812 \times 10^{-4}$
- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)

- Trace methyl nitrite features removed via spectral subtraction.
- Baseline correction via 7<sup>th</sup> order polynomial subtraction