

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for CH<sub>4</sub>\_5T

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

Equivalent concentration x path-length of composite spectrum:  $6.605 \times 10^{-7}$  grams/liter-meter

### **Sample Conditions-**

- Chemical name and CAS number: Methane, natural gas, methyl hydride, marsh gas, biogas, fire damp, CH<sub>4</sub>: [74-82-8]
- Physical properties: fw=16.0426 g/mole, fp=-182.5° C, bp=-161.5° C
- Supplier and stated purity: Matheson, 99%
- Sample class: I (PNNL scale).
- Temperature of sample:  $5.09 \pm 0.02$  C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples at 1.1278, 0.87334, 6.5603, 2.4181, 0.71884, 4.2845, 147.02, 105.45 and 61.48 Torr. Path length = 19.96 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 600 cm<sup>-1</sup> (1.534 to 16.667 microns)
- Instrumental resolution based on maximum interferometer displacement is 0.112 cm<sup>-1</sup>
- Spectral interval after 2X zero-filling interferogram and FFT: 0.06 cm<sup>-1</sup>
- 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<sup>-1</sup>

### **Post Processing and Related Parameters-**

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ( =0.90, =500)
- Composite spectrum created from 9 individual absorbance (base-10) spectra via classical least squares fit: Intercept=0, slope is fitted, individual absorbance values weighted by T<sup>2</sup> (transmission squared), all absorbance values > 1.6 are given zero weight
- Calculated and estimated errors: Type A = 0.89%, Type B = 3%
- Frequency correction (already applied):  $V(\text{corrected}) = V(\text{instrument}) * 0.999998 - 2.75000e-6$
- Axis units: X=wavenumbers (cm<sup>-1</sup>), Y=Absorbance (base-10)
- Trace carbon dioxide features removed via spectral subtraction. Some residual still observed
- Baseline correction via 7<sup>th</sup> order polynomial subtraction