

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for H<sub>2</sub>S\_25T

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

Equivalent concentration x path-length of composite spectrum:  $1.4031 \times 10^{-6}$  grams/liter-meter

Due to the extremely low cross-section associated with hydrogen sulfide and the similar vapor pressure curve with carbon dioxide, it was not possible to remove carbon dioxide features from the composite spectrum. Although the partial pressure of CO<sub>2</sub> was on the order of 0.1%, the high sample pressures required to observe H<sub>2</sub>S caused severe spectral contamination.

### Sample Conditions-

- Chemical name and CAS number: Hydrogen sulfide, sulfuretted hydrogen, hydrosulfuric acid, heptatic acid, sulfur hydride, stink damp, sour gas, sewer gas, H<sub>2</sub>S : [7783-06-4]
- Physical properties: fw=34.06 g/mole, fp=-83.3° C, bp=-60.2° C
- Supplier and stated purity: Spectra gases Inc., 98%
- Sample class: II (PNNL scale).
- Temperature of sample:  $25.07 \pm 0.02$  C
- Diluent: Sample back filled with ultra high purity nitrogen to  $760 \pm 5$  Torr
- Individual samples at 11.92, 215.92, 604.10, 398.80, 109.57, 50.28, 30.32 and 361.51 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at -120 C to remove air and minimize carbon dioxide.

### 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 ( $\alpha=0.90$ ,  $\beta=500$ )
- Composite spectrum created from 8 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 = 9.0%, Type B = 5%
- Frequency correction (already applied):  $V(\text{corrected}) = V(\text{instrument}) * 0.999998 + 1.287 \times 10^{-4}$

- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)
- Trace carbonyl sulfide and ethyl mercaptan features removed via spectral subtraction
- Baseline correction via 7<sup>th</sup> order polynomial subtraction