

All data taken at Pacific Northwest National Laboratory (PNNL)

Operators: Steven W. Sharpe, Timothy J. Johnson and Robert L. Sams : [sw.sharpe@pnl.gov](mailto:sw.sharpe@pnl.gov)

Version 1.0, May, 04

Composite spectrum for SO<sub>3</sub>\_25T

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

Equivalent concentration x path-length of composite spectrum: 3.296x10<sup>-6</sup> grams/liter-meter

Composite spectrum was created by appending data from mid-band MCT and wide-band-MCT detectors. Multiple spectral features due to reaction of windows (AgCl) with SO<sub>3</sub>. Removed “window” features by subtraction of selected “deviation” vector regions. Residual still observable in composite spectrum as “derivative” shaped features.

### Sample Conditions-

- Chemical name and CAS number: Sulfur trioxide, Sulfan, sulfuric anhydride, SO<sub>3</sub> : [7446-11-9]
- Physical properties: fw=80.0582 g/mole, fp=16.8° C, bp=44.8° C
- Supplier and stated purity: Aldrich, 99%, stabilized
- Sample class: III (PNNL scale). Extremely reactive
- Temperature of sample: 25.02 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples at:  
0.550, 1.40, 0.900, 2.300, 4.00, 9.00, 17.00 and 33.00 Torr (6500-565 cm<sup>-1</sup>)  
2.20, 4.50, 3.70, 1.70, 1.00 and 9.00 Torr (565-440 cm<sup>-1</sup>)
- Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at 77 K to remove air and SO<sub>2</sub>.

### 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 440 cm<sup>-1</sup> (1.534 to 22.727 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 ( $\alpha=0.85$ ,  $\epsilon=530$ )
- 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  $\geq 1.6$  are given zero weight
- Calculated and estimated errors: Type A = 3.50%, Type B  $\leq 10\%$

- 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  $\text{CO}_2$  vapor features removed via spectral subtraction
- Baseline correction via 7<sup>th</sup> order polynomial subtraction