

All data taken at Pacific Northwest National Laboratory (PNNL)
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Composite spectrum for SPCL3_5T

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

Equivalent concentration x path-length of composite spectrum: 6.974×10^{-6} grams/liter-meter

Lowest frequency band ($\sim 575 \text{ cm}^{-1}$) is near detector cut-off and susceptible to large detector non-linearity. This band may have significant intensity errors.

Sample Conditions-

- Chemical name and CAS number: Thiophosphoryl chloride, phosphorous sulfochloride, SPCl_3 : [3982-91-0]
- Physical properties: fw=169.40 g/mole, fp= -35° C , bp= 126° C
- Supplier and stated purity: Aldrich, 98%
- Sample class: II (PNNL scale). Unstable, hydrolyzes easily
- Temperature of sample: $4.92 \pm 0.02 \text{ C}$
- Diluent: Sample back filled with ultra high purity nitrogen to $760 \pm 5 \text{ Torr}$
- Individual samples at 1.08050, 0.44830, 2.5361, 0.83593, 1.5194 and 3.8850 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 cm^{-1} (1.534 to 19.048 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 ($\tau = 0.85$, $\nu = 530$)
- 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 = 2.22%, Type B = 5%
- Frequency correction (already applied): $V(\text{corrected}) = V(\text{instrument}) * 0.999997 + 5.18 \times 10^{-4}$
- Axis units: X=wavenumbers (cm^{-1}), Y=Absorbance (base-10)
- Trace hydrogen chloride features removed via spectral subtraction

- Baseline correction via 3rd order polynomial subtraction