

All data taken at Pacific Northwest National Laboratory (PNNL)
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Composite spectrum for TiCl₄_25T

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

Equivalent concentration x path-length of composite spectrum: 7.809x10⁻⁶ grams/liter-meter

Large *type-A* error due to poor signal-to-noise near 20 microns, the dominate absorption feature.

Sample Conditions-

- Chemical name and CAS number: Titanium tetrachloride, titanous chloride, T-4, titanium chloride, titanium(IV) chloride, TiCl₄ : [7550-45-0]
- Physical properties: fw=189.679 g/mole, fp=-30° C, bp=136.4° C
- Supplier and stated purity: Aldrich, 99.9%
- Sample class: I (PNNL scale).
- Temperature of sample: 25.01 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples at 1.07000, 5.2040, 8.1466, 7.3979, 6.7452, 8.5300, 3.1690 and 7.6639 Torr. Path length = 19.94 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at -50 C 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 500 cm⁻¹ (1.534 to 20.00 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 (=0.85, =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 T² (transmission squared), all absorbance values > 1.6 are given zero weight
- Calculated and estimated errors: Type A = 7.89%, Type B = 3%
- Frequency correction (already applied): V(corrected) = V(instrument)*0.999997+5.18x10⁻⁴
- Axis units: X=wavenumbers (cm⁻¹), Y=Absorbance (base-10)
- Trace hydrogen chloride features removed via spectral subtraction
- Baseline correction via 7th order polynomial subtraction