

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for NOCL_50T

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

Equivalent concentration x path-length of composite spectrum: 2.695×10^{-6} grams/liter-meter

Corrected for contamination of NO [2.9%], NO₂[0.17%] and HCl [0.38%]. Based on a comparison of the integrated areas for the 5, 25 and 50 C spectra, it appears that there may have been substantial [~7%] decomposition of the NOCl for the 50 C sample.

Sample Conditions-

- Chemical name and CAS number: Nitrosyl chloride, NOCl : [2696-92-6]
- Physical properties: fw=65.4591 g/mole, fp=-61.5° C, bp=-5.5° C
- Supplier and stated purity: Atomergic Chemicals Corp., 98%
- Sample class: II (PNNL scale). Extremely reactive. In equilibrium with NO + Cl₂
- Temperature of sample: 49.97 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples at 0.62500, 1.08400, 1.4580, 19.17, 9.0990 and 4.2130 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at -100 C to contaminants.

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 545 cm⁻¹ (1.534 to 18.349 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 6 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 = 1.58%, Type B = 5%
- Frequency correction (already applied): V(corrected) = V(instrument)* 0.99999896+8.812x10⁻⁴
- Axis units: X=wavenumbers (cm⁻¹), Y=Absorbance (base-10)
- Trace NO, NO₂, HCl and CO₂ features removed via spectral subtraction

- Baseline correction via 7th order polynomial subtraction