

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, September, 05

Composite spectrum for HMPA\_25T

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

Equivalent concentration x path-length of composite spectrum:  $7.3788 \times 10^{-6}$  grams/liter-meter

### Sample Conditions-

- Chemical name and CAS number: Hexamethylphosphoramide, hempa, hexamethylphosphoric acid triamide, tris(dimethylamino)phosphorous oxide, HMPA, HMPT, N,N,N,N,N,N-hexamethylphosphoric triamide : [680-31-9]
- Physical properties: MW=179.20146 g/mole, mp=7.2° C, bp=235° C, Density (20 C) 1.03 g/cm<sup>3</sup>
- Supplier and stated purity: Aldrich, 99%
- Sample class: I (PNNL scale).
- Temperature of White cell (796.0 cm optical path length)  $25 \pm 2$  C
- Diluent (high purity nitrogen) flowed at 24.2 liter/min (21.1° C), ambient atmospheric pressure  $760 \pm 5$  Torr.
- Samples flowed at 3.000, 1.000, 2.000, 0.800, 1.200, 1.800, 0.700, 3.500, 0.600, 4.000, 2.400, 2.200, 1.100, 4.500, 0.750 and 6.000 microliters/minute
- Individual samples at equivalent pressures of 0.013056, 0.004352, 0.008697, 0.003479, 0.005219, 0.007828, 0.003043, 0.015210, 0.002607, 0.017379, 0.010427, 0.009570, 0.004782, 0.019561, 0.003260 and 0.026071 Torr. Final data is a composite spectrum.
- Preparation: None

### Instrument Parameters-

- Bruker-66V FTIR, evacuated optics bench.
- Modified to include second aperture, between interferometer output and White cell. This substantially reduces both “ghosting” and warm aperture effects.
- Spectral range: 6,500 to 600 cm<sup>-1</sup> (1.538 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 ( $\alpha=0.90$ ,  $\epsilon=500$ )
- Composite spectrum created from 16 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 = 0.64%, Type B  $\leq$  7%
- Frequency correction (already applied):  $V(\text{corrected}) = V(\text{instrument}) * 0.99999959 - 3.45278 \times 10^{-4}$
- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)
- Trace water vapor features removed by spectral subtraction
- Baseline correction via 7<sup>th</sup> order polynomial subtraction