All data taken at the Pacific Northwest National Laboratory
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Composite spectrum for: Parathion

- First Column: Position in wavenumber (cm^{-1})
- Second column: Real refractive index $n(\tilde{\upsilon})$ (dispersion index)
- Third column: Imaginary refractive index, $k(\tilde{\upsilon})$ (absorption index per unit length in centimeters)

Where the complex refractive index $\hat{n} = n(\tilde{\upsilon}) + ik(\tilde{\upsilon})$

Following Bertie (in the references below) we define the absorbance as $A = -\log_{10}(I/I_0)$ and the linear absorption coefficient K = A/d, where d is the path length. The connection between the imaginary refractive index and the absorbance coefficient arises from the following: $2.303K = 4\pi\tilde{\upsilon}k$

See the following references for a detailed description of terms and units:

1) Bertie, J. E., Zhang, S. L., Eysel, H. H., Baluja, S., & Ahmed, M. K. (1993). Infrared Intensities of Liquids XI: Infrared Refractive Indices from 8000 to 2 cm^{-1}, Absolute Integrated Intensities, and Dipole Moment Derivatives of Methanol at 25°C. *Appl. Spec.,47*(8), 1100-1114 doi:10.1366/0003702934067973
2) Bertie, J. E., Zhang, S. L., & Keefe, C. D. (1995). Measurement and use of absolute infrared absorption intensities of neat liquids. *Vibrational Spectroscopy, 8*(2), 215-229. doi:10.1016/0924-2031(94)00038-i

Sample:

- Chemical name, formula and CAS number: Parathion, $C_{10}H_{14}NO_5PS$, [56-38-2]
- IUPAC name: *O*,*O*-Diethyl *O*-(4-nitrophenyl) phosphorothioate
- Synonyms: Ethylparathione; Parathion-ethyl
- Physical properties: FW = 291.26 g/mole; mp = 6.1 °C; bp = 707 °C; $\rho = 1.268$ g/cm^3
- Supplier and stated purity: Toronto Research Chemicals (TRC), 98% (Lot # 1-JHL-59-10)
- Temperature of sample: 25 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: MIR: 5.7, 6.5, 7.3, 7.6, 13.6, 24.5, 55.9, 92.8, 189 and 498 micrometers (µm); NIR: 94.5, 192, 504 and 960 µm. Final data are a composite of these spectra.
- Sample cell window material: MIR = potassium bromide (KBr) except potassium chloride (KCl) for the 7.6 and 498 µm cells; NIR = KCl except KBr for the 504 µm cell.
- Preparation: None

NIR Instrument Parameters:

- Bruker Vertex 70, purged with UHP nitrogen
- Spectral range: 10,000 to 3,000 cm^{-1} (1.0 to 3.33 microns)
- NIR source: Quartz tungsten bulb
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 15801 to 0 cm^{-1}

MIR Instrument Parameters:

- Tensor 37, purged with UHP nitrogen
- Spectral range: 7800 to 400 cm^{-1} (1.282 to 25 microns)
- NIR source: Silicon carbide glow bar
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 15802 to 0 cm^{-1}

NIR/MIR Instrument Parameters:

- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10 kHz; 7.5 kHz (new MIR)
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4822 cm^{-1}

a) b)

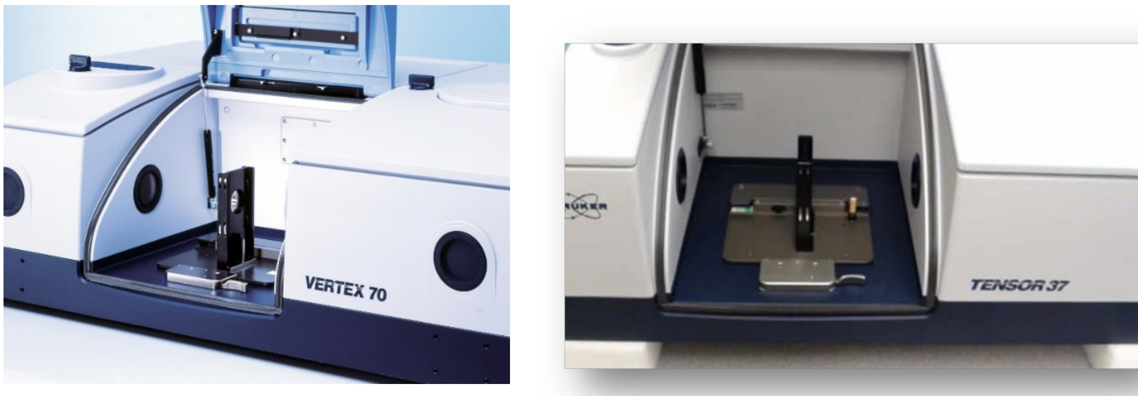

Figure 1: The Bruker Vertex 70 FTIR (a) and Tensor 37 (b).

Measured Refractive Index:

The refractive index for Parathion was measured at 25 °C using an Atago model DR-M2/1550 Abbe refractometer. Notch filters were employed in front of a white light source to make measurements at multiple wavelengths. An infrared viewer from Atago was used to detect signal at 1550 nm. The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm:	n = 1.5499	486 nm:	n = 1.5489	546 nm:	n = 1.5384
589 nm:	n = 1.5331	644 nm:	n = 1.5279	656 nm:	n = 1.5267
1550 nm:	n = 1.5067				

The refractive index, *n*, vs. wavelength in microns, λ, was fit to an equation similar to that of Sellmeier:

$$n(\lambda) = \{a + b/(\lambda^2 - c)\}^{1/2}$$

The resulting best-fit equation was used to find the refractive index at the highest energy data points in our experimental spectra. For Parathion, the results were

$n(7{,}800\ cm^{-1}) = 1.5086$ at 25 °C for MIR data and
$n(10{,}000\ cm^{-1}) = 1.5127$ at 25 °C for NIR and merged data.

Post Processing and Related Parameters:
For the MIR, a composite spectrum was created from 10 absorbance spectra (base-10) taken at 10 path lengths: 5.7, 6.5, 7.3, 7.6, 13.6, 24.5, 55.9, 92.8, 189 and 498 micrometers (µm). For the NIR, a composite spectrum was created from 4 absorbance spectra (base-10) taken at 4 path lengths: 94.5, 192, 504 and 960 µm. At each path length several spectra were measured and the results averaged for better signal to noise. The measured cell lengths were adjusted using Beer's law plots in which the NIR and MIR data were analyzed independently.

1) The imaginary part of the refractive index, or *k* vector, was determined for each absorbance file as per Bertie's program "RNJ46A" (see reference above). This takes into account the reflective losses due to the KBr and/or KCl windows.
2) A composite *k* vector is created via a classical, weighted, linear, least squares fit using the output files of program "RNJ46A": Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values ≥ 2.5 are given zero weight. For the MIR, ten composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 189 and 498 µm cells. This *k* vector determined the final values for the range from 7800 to 4706 cm^{-1}.
   b) The second *k* vector used the results from the 92.8 through 498 µm cells. This *k* vector determined the final values for the range from 4706 to 3130 cm^{-1} and 2900 to 1620 cm^{-1}.
   c) The third *k* vector used the results from the 7.3 and 13.6 through 55.9 µm cells. This *k* vector determined the final values for the range from 3130 to 2900 cm^{-1}.
   d) The fourth *k* vector used the results from the 5.7 through 13.6 µm cells. This *k* vector determined the final values for the range from 1620 to 1610 cm^{-1}.
   e) The fifth *k* vector used the results from the 5.7, 6.5 and 7.6 µm cells. This *k* vector determined the final values for the range from 1610 to 1485 cm^{-1} and 1360 to 1340 cm^{-1}.
   f) The sixth *k* vector used the results from the 13.6, 24.5 and 55.9 µm cells. This *k* vector determined the final values for the range from 1485 to 1360 cm^{-1} and 1340 to 1250 cm^{-1}.
   g) The seventh *k* vector used the results from the 5.7, 6.5, 7.6 and 13.6 µm cells. This *k* vector determined the final values for the range from 1250 to 1200 cm^{-1}.
   h) The eighth *k* vector used the results from the 5.7, 6.5, 7.3,13.6 and 24.5 µm cells. This *k* vector determined the final values for the range from 1200 to 1150 cm^{-1}.
   i) The ninth *k* vector used the results from the 5.7 and 6.5 µm cells. This *k* vector determined the final values for the range from 1150 to 750 cm^{-1}.
   j) The tenth *k* vector used the results from the 5.7 and 6.5 µm cells. This *k* vector determined the final values for the range from 750 to 400 cm^{-1}.
3) A frequency correction was applied to the resulting composite MIR *k* vector.
   a) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * 0.999888 – 0.0002] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
4) For the NIR, three composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 504 and 960 µm cells. This *k* vector determined the final values for the range from 10,000 to 6100 cm^{-1}.
   b) The second *k* vector used the results from all the path lengths. This *k* vector determined the final values for the range from 6100 to 4460 cm^{-1}.
   c) The third *k* vector used the results from the 192 and 504 µm cells. This *k* vector determined the final values for the range from 4460 to 400 cm^{-1}.
5) The resulting composite NIR *k* vector and the refractive index at 10,000 cm^{-1} were used to create the real or *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
   a) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * 0.999976 – 0.0005] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
6) The MIR data were mapped onto the NIR x-axis using an interpolation routine, i.e. the Make Compatible command in OPUS 5.5. Then the composite MIR and NIR *k* vectors were merged to generate a final composite *k* vector across the entire spectral range. The NIR data were used exclusively above 3016 cm^{-1}, and only the MIR data were used below 3010 cm^{-1}. A weighted average, with the weight of the MIR

vector increasing linearly from 0 to 100% between 3016 and 3010 cm^{-1} was used in the overlapping spectral region. The resulting composite *k* vector and the refractive index at 10,000 cm^{-1} were used to create the final *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."

Photograph of Sample Parathion:

Figure 2: Parathion in TRC containers for NIR and MIR measurements.