

All data taken at the Pacific Northwest National Laboratory

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Composite spectrum for: Malathion

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

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

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: $2.303K = 4\pi\tilde{\nu}k$

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: Malathion, $\text{C}_{10}\text{H}_{19}\text{O}_6\text{PS}_2$, [121-75-5]
- IUPAC name: Diethyl[dimethoxyphosphinothioylthio]butanedioate
- Synonyms: Diethyl (dimethoxyphosphinothioylthio) succinate; *S*-[1,2-Bis(ethoxycarbonyl)ethyl] *O,O*-dimethyl-phosphorodithioate; 1,2-Di(ethoxycarbonyl)ethyl-*O,O*-dimethylphosphorodithioate
- Physical properties: FW = 330.36 g/mole; mp = 3°C ; bp = $156 - 157^\circ\text{C}$; $\rho = 1.23\text{ g/cm}^3$
- Supplier and stated purity: MIR = Pfaltz and Bauer, 95% (Lot # 122029-1); NIR = Toronto Research Chemicals (TRC), 97% (Lot # 4-ABY-188-1)
- Temperature of sample: 27°C ($\pm 1^\circ\text{C}$)
- Individual samples were measured at the following path lengths: MIR = 6.2, 10.7, 25.4, 47.6, 107, 196, and $500\text{ }\mu\text{m}$; NIR = 129, 206, 530, 2089 and $3961\text{ }\mu\text{m}$. Final data are a composite of these spectra.
- Sample cell window material: MIR = potassium bromide (KBr); NIR = potassium chloride (KCl) except for the 129 and $206\text{ }\mu\text{m}$ cells.
- Preparation: None

NIR Instrument Parameters:

- Bruker Vertex 70, purged with UHP nitrogen
- Spectral range: $10,000$ to $3,000\text{ cm}^{-1}$ (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:

- Bruker Vector 33, purged with UHP nitrogen
- Spectral range: $7,800$ to 400 cm^{-1} (1.282 to 25 microns)
- IR source: Silicon carbide glow bar
- Beamsplitter: Potassium bromide (KBr)
- Detector: DTGS at room temperature
- Aperture: 3 mm
- Folding limits: 15798 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
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.482 cm^{-1}

a)



b)



Figure 1: The Bruker Vertex 70 FTIR (a) and Bruker Vector 33 FTIR (b).

Measured Refractive Index:

The refractive index for Malathion was measured at $25\text{ }^{\circ}\text{C}$ 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:	$n = 1.5053$	486 nm:	$n = 1.5052$	546 nm:	$n = 1.5000$
589 nm:	$n = 1.4971$	644 nm:	$n = 1.4951$	656 nm:	$n = 1.4940$
1550 nm:	$n = 1.4756$				

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 Malathion, the results were

$$\begin{aligned} n(7,800\text{ cm}^{-1}) &= 1.4780 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for MIR data and} \\ n(10,000\text{ cm}^{-1}) &= 1.4824 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for NIR and merged data.} \end{aligned}$$

Post Processing and Related Parameters:

For the MIR, a composite spectrum was created from 7 absorbance spectra (base-10) taken at 7 path lengths: 6.2, 10.7, 25.4, 47.6, 107, 196 and 500 micrometers (μm). For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 129, 206, 530, 2089 and 3961 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, five composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 500 μm cell. This k vector determined the final values for the range from 7800 to 3050 and 2828 to 1879 cm^{-1} .
 - b) The second k vector used the results from the 107, 196 and 500 μm cells. This k vector determined the final values for the range from 1706 to 1494 and 562 to 400 cm^{-1} .
 - c) The third k vector used the results from the 25.4, 47.6, 107, 196 and 500 μm cells. This k vector determined the final values for the range from 3050 to 2828 and 1879 to 1816 cm^{-1} .
 - d) The fourth k vector used the results from the 10.7, 25.4, 47.6, 107, 196 and 500 μm cells. This k vector determined the final values for the range from 1816 to 1752, 1720 to 1706, 1494 to 1157 and 838 to 562 cm^{-1} .
 - e) The fifth k vector used the results from all the cells. This k vector determined the final values for the range from 1752 to 1720 and 1157 to 838 cm^{-1} .
- 3) A frequency correction was applied to the resulting composite MIR k vector.
 - a) Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 1.00003 + 0.185411]$ 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, two composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 2089 and 3961 μm cells. This k vector determined the final values for the range from 10,000 to 6500 cm^{-1} .
 - b) The second k vector used the results from the 129 through 3961 μm cells. This k vector determined the final values for the range from 6500 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): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.999748 + 0.00481475]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 6) Finally, 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 3250 cm^{-1} , and only the MIR data were used below 3150 cm^{-1} . A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 3150 and 3250 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 Malathion:

No photo available of Malathion in Pfaltz and Bauer container used for MIR measurements.



Figure 2: Malathion in Toronto Research Chemicals (TRC) container for NIR measurements.