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

- 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. *Applied Spectroscopy, 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: Trimethyl phosphate, $C_3H_9O_4P$, [512-56-1]
- IUPAC name: Trimethyl phosphate
- Synonyms: TMP; Phosphoric acid trimethyl ester; Trimethoxy phosphine oxide; Trimethyl orthophosphate
- Physical properties: FW = 140.076 g/mole; mp = -46 °C; bp = 197 °C; ρ = 1.197 g/cm^3
- Supplier and stated purity: Aldrich, ≥98% (Lot # 73496JM)
- Temperature of sample: 26 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: 1.9, 2.6, 3.2, 4.1, 9.8, 14.4, 15.5, 35.9, 51.4, 97.2, 200, 503 and 1042 micrometers (μm). Final data are a composite of these spectra.
- Sample cell window material is potassium bromide (KBr).
- Preparation: None.

Instrument Parameters:

- Bruker Vertex 70 FTIR, purged with UHP nitrogen
- Spectral range: 7800 to 400 cm^{-1} (1.282 to 25 microns)
- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10kHz
- Folding limits: 15800 to 0 cm^{-1}
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.48213 cm^{-1}
- IR source: Silicon carbide glow bar
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 4 mm

Measured Refractive Index:
The refractive index for TMP was measured at 27 °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 InGaAs camera 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 = 1.3986	486 nm: n = 1.3983	546 nm: n = 1.3953
589 nm: n = 1.3939	644 nm: n = 1.3925	656 nm: n = 1.3920
1550 nm: n = 1.3853		

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 point in our experimental spectra. For trimethylphosphate, the result was

$$n(7800\ cm^{-1}) = 1.3860 \text{ at } 27\ °C.$$

a) b)

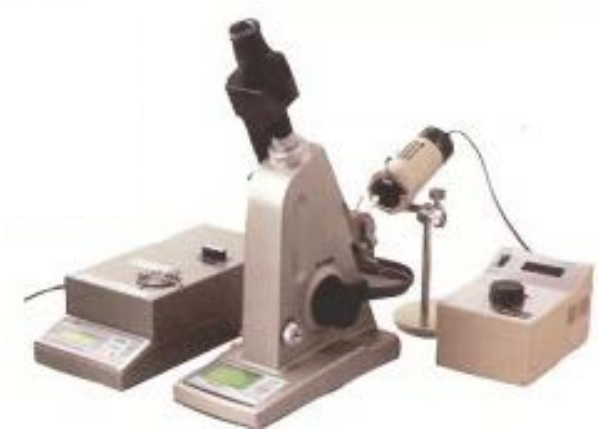

Figure 1: The Bruker Vertex 70 FTIR (a) and Abbe refractometer (b).

Post Processing and Related Parameters:
A composite spectrum was created from 10 absorbance spectra (base-10) taken at 13 path lengths: 1.9, 2.6, 3.2, 4.1, 9.8, 14.4, 15.5, 35.9, 51.4, 97.2, 200, 503 and 1042 micrometers (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.

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 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. Six composite vectors were created and merged by hand.
    a) The first k vector used the results from the 1042 and 503 μm cells. This k vector determined the final values for the range from 7800 to 4800 cm^{-1}.
    b) The second k vector used the results from the 200 through 34 μm cells. This k vector determined the final values for the range from 4800 to 3040 cm^{-1}.

c) The third *k* vector used the results from the 36, 15, 13, 10, and 3 μm cells. This *k* vector determined the final values for the range from 3040 to 2800 cm^{-1}.
d) The fourth *k* vector used the results from the 200 through 15 μm cells. This *k* vector determined the final values for the range from 2800 to 1600 cm^{-1}.
e) The fifth *k* vector used the results from the 1 through 10 μm cells. This *k* vector determined the final values for the range from 1600 to 600 cm^{-1}.
f) The final *k* vector used the results from the 10 through 51 um cells. This *k* vector determined the final values for the range from 600 to 400 cm^{-1}.

3) The resulting composite *k* vector and the refractive index at 7800 cm^{-1} were used to create the real or *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
a) Calculated and estimated errors: Type A = 0.7%.
b) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * .99996 - .078212] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
c) Axis units: X = Wavenumbers (cm^{-1}); Y = Absorbance (base 10).

Photograph of Sample Trimethyl Phosphate:

Figure 2: Trimethyl phosphate in Aldrich container.