All data taken at the Pacific Northwest National Laboratory
FTS Operators: John S. Loring, Ashley M. Bradley and Russell G. Tonkyn
Data Analysis: Russell G. Tonkyn

Composite spectrum for: Silicone oil

- 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: Silicone oil, $[-Si(CH_3)_2O-]_n$, [63148-62-9]
- IUPAC name: Silicone oil
- Synonyms: Polydimethylsiloxane
- Physical properties: FW = n/a; mp = -55 °C; bp = 341 °C; $\rho = 0.97$ g/cm^3
- Supplier and stated purity: MIR: Sigma-Aldrich for oil baths, purity not available (Lot # BCBQ2271V); NIR: Alfa Aesar, purity not available (Lot # 10219671).
- Temperature of sample: 26 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: MIR: 0.98, 5.04, 9.84, 16.8, 23.1, 31.2, 56.5, 101, 201, 532 and 1006 micrometers (μm); NIR: 101, 197, 502, 985 and 3974 μm. Final data are a composite of these spectra.
- Sample cell window material is potassium bromide (KBr) except for the 101, 197, 502 and 985 μm cells which are made with quartz and the 3974 μm cell which is made with potassium chloride (KCl).
- Preparation: None

NIR Instrument Parameters:

- Bruker Vertex 70, purged with UHP nitrogen
- Spectral range: 10,000 to 400 cm^{-1} (1.0 to 25 microns)
- IR source: Quartz tungsten bulb
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 31604.8 to 0 cm^{-1}

MIR Instrument Parameters:

- Tensor 27, purged with UHP nitrogen
- Spectral range: 7,800 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
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4823 cm^{-1}

a) b)

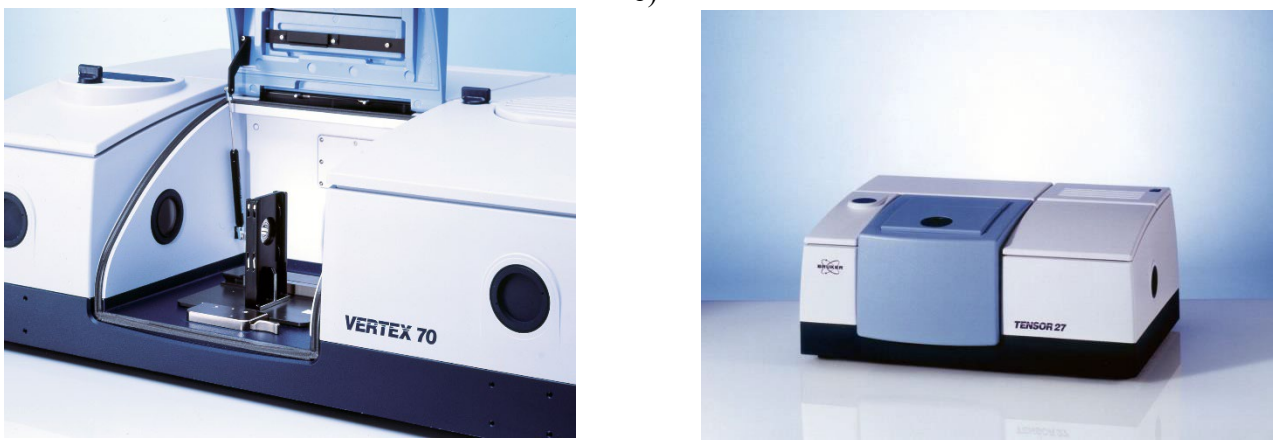

Figure 1: The Bruker Vertex 70 FTIR (a) and Tensor 27 FTIR (b).

Measured Refractive Index:

The refractive index for silicone oil 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 = 1.4077	486 nm: n = 1.4072	546 nm: n = 1.4034
589 nm: n = 1.4021	644 nm: n = 1.3996	656 nm: n = 1.3994
1550 nm: n = 1.3823		

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 silicone oil, the results were

n(7,800 cm^{-1}) = 1.3848 at 25 °C for MIR data and
n(10,000 cm^{-1}) = 1.3891 at 25 °C for NIR and merged data.

Post Processing and Related Parameters:
For the MIR, a composite spectrum was created from 11 absorbance spectra (base-10) taken at 11 path lengths: 0.98, 5.04, 9.84, 16.8, 23.1, 31.2, 56.5, 101, 201, 532 and 1006 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. For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 101, 197, 502, 985 and 3974 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, KCl, and/or Quartz 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 data from the 1006 and 532 μm pathlength cells. This *k* vector determined the final values for the range from 7800 to 3213 cm^{-1} and from 471 to 400 cm^{-1}.
   b) The second *k* vector used data from the 201 and 101 μm pathlength cells. This *k* vector determined the final values for the range from 3213 to 2983 cm^{-1}.
   c) The third *k* vector used data from the 56.5 and 31.2 μm pathlength cells. This *k* vector determined the final values for the range from 2983 to 2972 cm^{-1} and from 2956 to 1342 cm^{-1}.
   d) The fourth *k* vector used data from the 23.1 and 16.8 μm pathlength cells. This *k* vector determined the final values for the range from 1342 to 1268 cm^{-1}, from 1186 to 1138 cm^{-1}, from 995 to 826 cm^{-1} and from 788 to 471 cm^{-1}.
   e) The fifth *k* vector used data from the 5.04 and 0.98 μm pathlength cells. This *k* vector determined the final values for the range from 2972 to 2956 cm^{-1}, from 1268 to 1186 cm^{-1}, from 1138 to 995 cm^{-1} and from 826 to 788 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) * 0.99977 – 0.01872] 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, four composite vectors were created and merged by hand.
   a) The first *k* vector used data from the 985 and 3974 μm pathlength cells. This *k* vector determined the final values for the range from 10,000 to 7600 cm^{-1}.
   b) The second *k* vector used data from the 197, 502, 985 and 3974 μm pathlength cells. This *k* vector determined the final values for the range from 7600 to 6800 cm^{-1}.
   c) The third *k* vector used data from all the pathlength cells. This *k* vector determined the final values for the range from 6800 to 4800 cm^{-1}.
   d) The fourth *k* vector used data from the 101, 197, 502 and 985 μm pathlength cells. This *k* vector determined the final values for the range from 4800 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) * 0.999748 + 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 3300 cm^{-1}, and only the MIR data were used below 3200 cm^{-1}. A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 3300 and 3200 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 silicone oil:

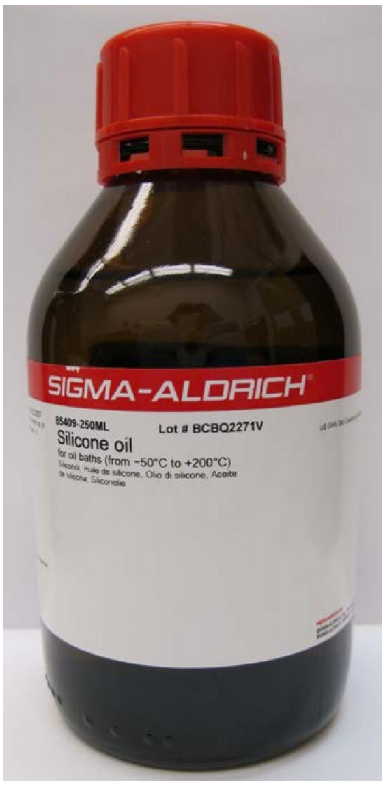

Figure 2: Silicone oil in Sigma-Aldrich container for MIR measurements.

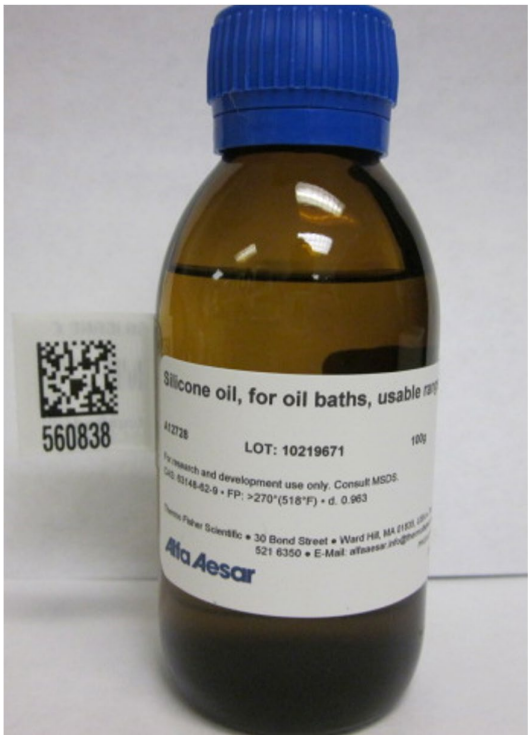

Figure 3: Silicone oil in Alfa Aesar container for NIR measurements.