All data taken at the Pacific Northwest National Laboratory
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Data Analysis: Russell G. Tonkyn

Composite spectrum for: Methanol

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

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

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

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: Methanol, CH_4O, [67-56-1]
- IUPAC name: Methanol
- Synonyms: Methyl Alcohol; Wood alcohol
- Physical properties: FW = 32.04 g/mole; mp = -98 °C; bp = 64.7 °C; ρ = 0.791 g/cm^3
- Supplier and stated purity: MIR: Sigma-Aldrich, 99.8% (Lot # SHBG6650V); NIR: Sigma-Aldrich, 99.8% (Lot # SHBL3263)
- Temperature of sample: 26 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: MIR: 6.89, 14.8, 30.4, 55.7, 101, 205, 545 and 1021 µm; NIR: 99.2, 201, 492, 1012 and 2120 µm. Final data are a composite of these spectra.
- Sample cell window material is potassium bromide (KBr) except for the 1012 and 2120 µm cells which are potassium chloride (KCl)
- 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)
- 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}

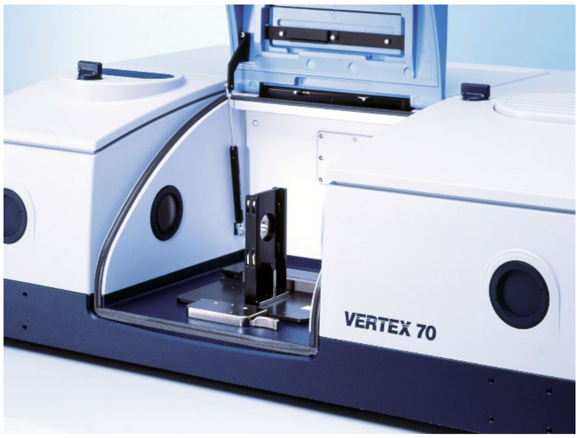
MIR Instrument Parameters:

- 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)

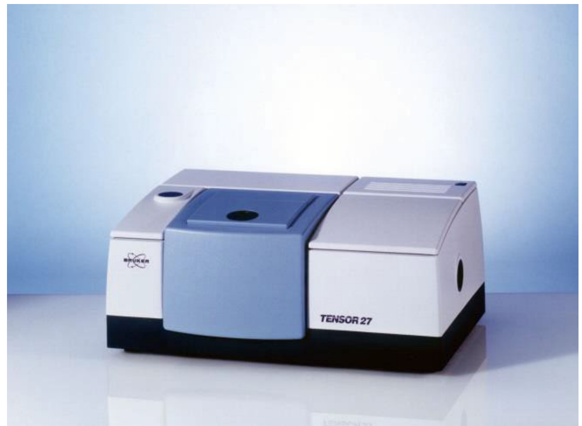


Figure 1: The Bruker Vertex 70 FTIR (a) and Tensor 27 FTIR (b).

Measured Refractive Index:

The refractive index for Methanol 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 = 1.3307	486 nm: n = 1.3300	546 nm: n = 1.3278
589 nm: n = 1.3267	644 nm: n = 1.3257	656 nm: n = 1.3245
1550 nm: n = 1.3107		

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 Methanol, the results were

$n(7,800\ cm^{-1}) = 1.3131$ at 25 °C for MIR data and
$n(10,000\ cm^{-1}) = 1.3170$ at 25 °C for NIR and merged data.

Post Processing and Related Parameters:
For the MIR, a composite spectrum was created from 8 absorbance spectra (base-10) taken at 8 path lengths: 6.89, 14.8, 30.4, 55.7, 101, 205, 545 and 1021 micrometers (µm). For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 99.2, 201, 492, 1012 and 2120 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, four composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 1021 and 545 µm cells. This *k* vector determined the final values for the range from 7800 to 4511 cm^{-1}.
   b) The second *k* vector used the results from the 205 and 101 µm cells. This *k* vector determined the final values for the range from 4511 to 3701 cm^{-1}.
   c) The third *k* vector used the results from the 55.7 and 30.4 µm cells. This *k* vector determined the final values for the range from 3701 to 3656 cm^{-1} and 919 to 400 cm^{-1}.
   d) The fourth *k* vector used the results from the 14.8 and 6.89 µm cells. This *k* vector determined the final values for the range from 2699 to 919 cm^{-1}.
   e) Results from the shortest path length cell (6.89 µm) had to be used exclusively for the region from 3656 to 2699 cm^{-1} because even those from the second shortest cell were saturated, precluding the use of any of the merged vectors.
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, two composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 1012 and 2120 µm cells. This *k* vector determined the final values for the range from 10,000 to 7500 cm^{-1}.
   b) The second *k* vector used the results from the 99.2 through 2120 µm cells. This *k* vector determined the final values for the range from 7500 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 + 0.0048] 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 3700 cm^{-1}, and only the MIR data were used below 3640 cm^{-1}. A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 3700 and 3640 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."

Photographs of Sample Methanol:

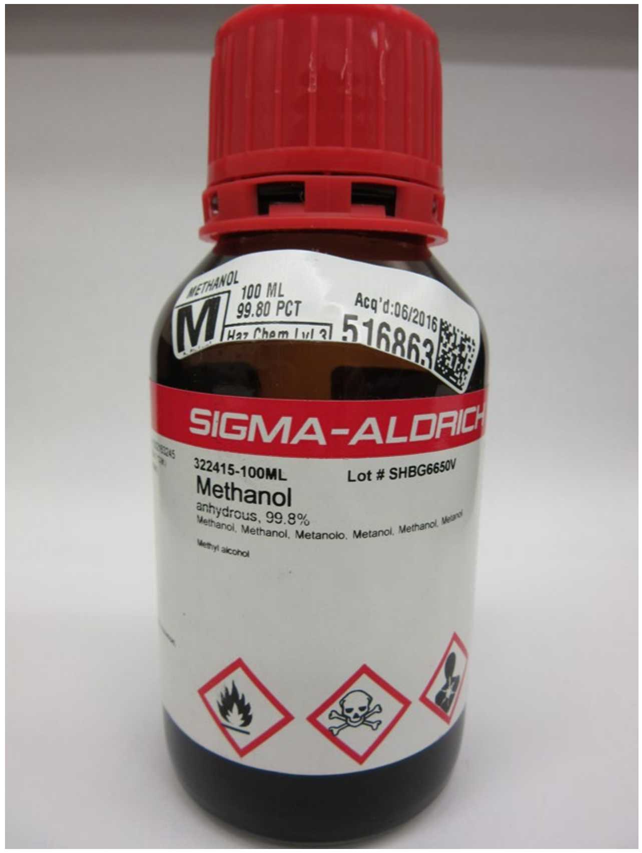


Figure 2: Methanol in Sigma-Aldrich container for MIR measurements.

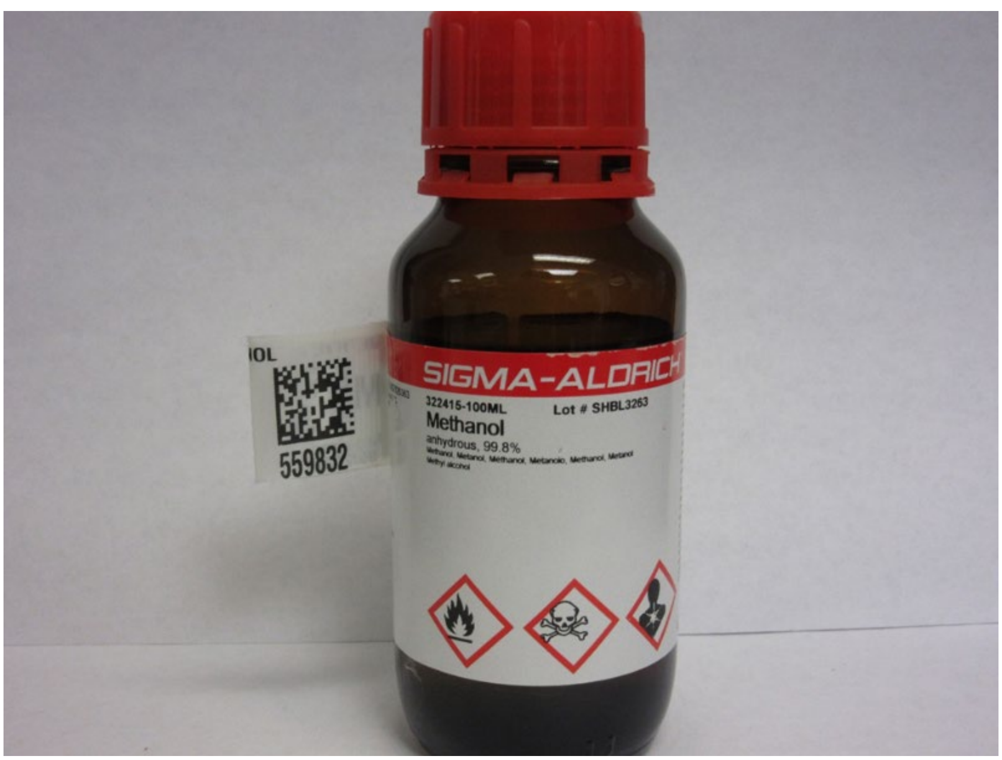


Figure 3: Methanol in Sigma-Aldrich container for NIR measurements.