

All data taken at the Pacific Northwest National Laboratory

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Composite spectrum for: Ammonium hydroxide solution, 29%

- 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
- 3) Bertie, J. E., & Lan, Z. (1996). An accurate modified Kramers–Kronig transformation from reflectance to phase shift on attenuated total reflection. *J. Chem. Phys.*, 105(19), 8502-8514. doi:10.1063/1.472635

Sample:

- Chemical name, formula and CAS number: Ammonium hydroxide, NH_4OH , [1336-21-6]
- IUPAC name: Ammonium hydroxide
- Synonyms: Ammonia water; Ammonia aqueous; Ammonia solution
- Physical properties: FW = 35.05 g/mole; mp = -60°C ; bp = $38\text{--}100^\circ\text{C}$; $\rho = 0.9\text{ g/cm}^3$
- Supplier and stated purity: MIR = Fisher Scientific, 29.2% (Lot # 983775); NIR = Alfa Aesar, 28.66% (Lot # R06G070)
- Temperature of sample: 27°C ($\pm 1^\circ\text{C}$)
- Individual samples were measured at the following path lengths: MIR = 7.85 reflections in Germanium (Ge) circle cell; NIR = 101, 197, 506, 994 and $2019\text{ }\mu\text{m}$. Final data are a composite of these spectra.
- Sample cell window material: MIR = Germanium (Ge); NIR = quartz
- 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 22, purged with UHP nitrogen
- Spectral range: 5020 to 675 cm^{-1} (1.99 to 14.8 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: MIR = 32; NIR = 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: MIR = 2.2 kHz; NIR = 10 kHz
- Interferogram zerofill: MIR = 2x; NIR = 4x
- Spectral interval after zerofilling: MIR = 0.964 cm^{-1} ; NIR = 0.482 cm^{-1}

a)



b)

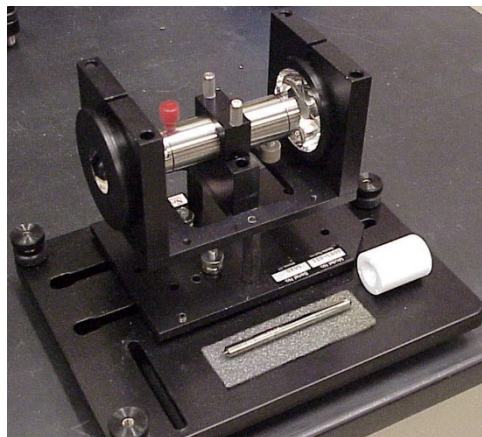


Figure 1: The Bruker Vertex 70 FTIR (a) and ATR accessory used with Bruker Vector 22 FTIR (b).

Measured Refractive Index:

The refractive index for Ammonium hydroxide solution 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: $n = 1.3494$	486 nm: $n = 1.3492$	546 nm: $n = 1.3460$
589 nm: $n = 1.3446$	644 nm: $n = 1.3431$	656 nm: $n = 1.3420$
1550 nm: $n = 1.324$		

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 Ammonium hydroxide solution, the results were

$$\begin{aligned} n(7800\text{ cm}^{-1}) &= 1.3271 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for MIR data and} \\ n(10,000\text{ cm}^{-1}) &= 1.3321 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for NIR and merged data.} \end{aligned}$$

Post Processing and Related Parameters:

Modifications to the standard experimental procedure in the MIR were required for ammonium hydroxide due to its aqueous nature and reactivity. Salt cells such as KBr or KCl could not be utilized. The spectra were instead obtained using an attenuated reflection (ATR) accessory. Bertie's program "PKREF" was used to determine the k vector. The number of optical reflections or "bounces" in the ATR accessory was calibrated using pure water by adjusting the value until agreement with Bertie's reference spectrum was achieved. The n vector was calculated from the k vector using Bertie's program "LZZKTB." For information on the use of ATR to obtain optical constants, see reference 3. The FORTRAN programs are available on Bertie's website along with a discussion of their use.

- 1) The imaginary or k -vector was determined for each absorbance file as per Bertie's program "PKREF" (see references above). This takes into account the wavelength dependent refractive index of the germanium crystal. The number of reflections was determined by comparing the k -vector calculated for H₂O with the reference file downloaded from John Bertie's download site (<https://sites.ualberta.ca/~jbertye/JBDownload.HTM>). The number of reflections was adjusted to obtain the closest match to the reference spectrum. A fresh calibration water spectrum was taken immediately prior to taking the spectra. The real n -vector was determined for each absorbance spectrum with the same PKREF program.
- 2) The composite k and n vectors were created by a simple arithmetic average of the output of "PKREF."
 - a) The reported data were obtained from 2 individual absorbance (base-10) spectra taken with a germanium crystal in the circle cell. The natural absorbance of germanium limited the available spectral range to between 5020 and 875 cm⁻¹.
- 3) A frequency correction was applied to the resulting composite MIR k vector.
 - a. Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 1.000047 + 0.170856]$ as determined by comparing measured atmospheric spectral lines (H₂O and CO₂) to values from the Northwest Infrared Spectral Library Database.

For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 101, 197, 506, 994 and 2019 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.

- 4) 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.
- 5) 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 T² (transmission squared), all absorbance values ≥ 2.5 are given zero weight. For the NIR, three composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 994 and 2019 μm cells. This k vector determined the final values for the range from 10,000 to 7200 cm⁻¹.
 - b) The second k vector used the results from the 101 through 2019 μm cells. This k vector determined the final values for the range from 7200 to 5500 cm⁻¹.
 - c) The third k vector used the results from the 101 and 197 μm cells. This k vector determined the final values for the range from 5500 to 400 cm⁻¹.
- 6) 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 (H₂O and CO₂) to values from the Northwest Infrared Spectral Library Database.
- 7) 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 3687 cm⁻¹, and only the MIR data were used below 3683 cm⁻¹. A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 3687 and 3683 cm⁻¹ was used in the

overlapping spectral region. The resulting composite k vector and the refractive index at $10,000\text{ cm}^{-1}$ were used to create the final n vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."

Photograph of Sample Ammonium hydroxide solution:

No photo available of Ammonium hydroxide solution in Fisher Scientific container used for MIR measurements.

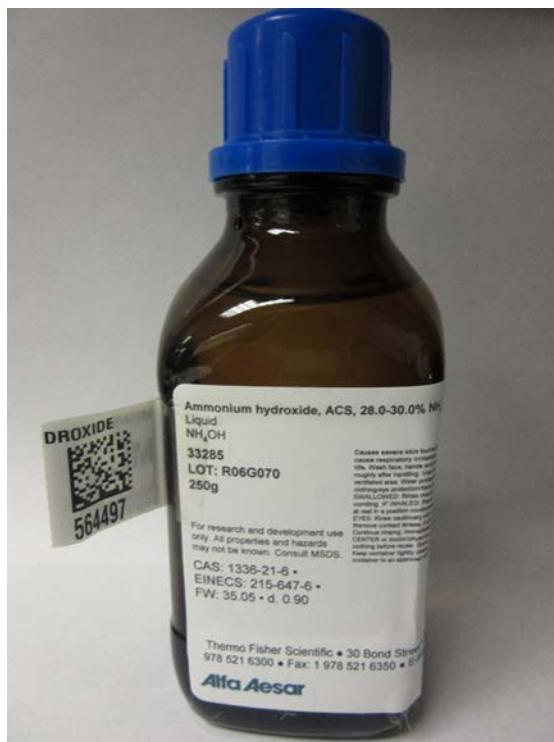


Figure 2: Ammonium hydroxide solution, 28-30%, in Alfa Aesar container for NIR measurements.