Choice of Window Materials for Transmission Sampling of Liquids in the Mid-IR Spectral Region

Measurement of liquid samples or samples dissolved in aqueous or organic solvents in the infrared (IR) spectral region is often done using a liquid cell of either fixed or variable pathlength. The liquid cell may be of sealed construction where windows are amalgamated together with a spacer to define the sampling pathlength, or it may be of a demountable design where the user can freely change sampling pathlength or window material. In the case of a neat, liquid sample that is somewhat viscous and the sampling pathlength does not need to be reproduced, we can simply press the liquid sample between 2 infrared transparent windows and collect the IR spectrum.

The choice of the IR transparent window material for liquid samples depends upon many factors including spectral range, refractive index, water solubility, hardness, melting point and pH range. Numerical values for these characteristics for many of the crystal materials used in the mid-IR spectral region are shown in Table 1, Properties of Materials for Mid-IR Spectroscopy shown on page 3 of this document.

Further useful information can be obtained by examining the spectra of these materials. Spectral data will show relative IR throughput for the material, any additional spectral features which could make sample identification more difficult and show useful spectral range for a given crystal thickness. We have run 2 mm thick samples of these materials for your reference and review. All spectra were collected at 4 cm-1 spectral resolution in the focused beam of the FTIR spectrometer. Data were collected within the spectral range of 7000 to 350 cm-1. Figures 1 through 3 are displayed to exhibit the long wavelength cutoff and any additional spectral absorbance bands. These spectra are shown in 3 sets. The first set shown in Figure 1, includes materials which are water soluble to slightly water soluble as detailed in Table 1.

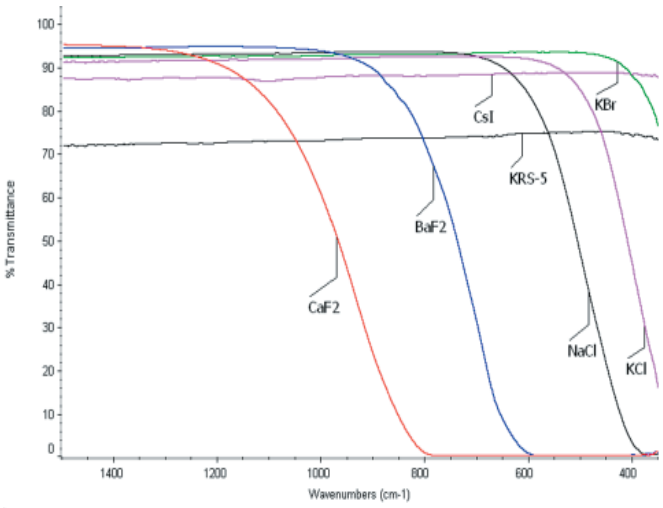

Figure 1. Transmission FTIR spectra for 2 mm thick windows of CaF_2, BaF_2, NaCl, KCl, CsI and KBr.

Within set 1 of materials, KBr is very popular because of its wide spectral range and relative low cost for use with organic samples and organic solvents. It is not recommended for use with low molecular weight alcohols or glycols as it is very hygroscopic and will absorb water from these solvents.

Set 2 of materials for IR transmission measurements in the mid-IR spectral region includes those materials which are not soluble in water and their spectra are shown in Figure 2. Of these materials, ZnSe is the most popular because of its relatively wide spectral range and its relative freedom from IR absorbance bands within the mid-IR spectral region. This is contrasted with Ge and Si, both of which exhibit absorbance bands at wavenumber values above their spectral cutoff. These absorbance bands can be difficult to subtract or ratio if they are too intense due to a combination of sur-

face reflections and refractive index effects. An additional benefit of ZnSe as a transmission material for FTIR is its visible transparency, providing the assurance of sample positioning within a cell. That benefit is not available for Ge, Si, or AMTIR because their refractive index is too high.

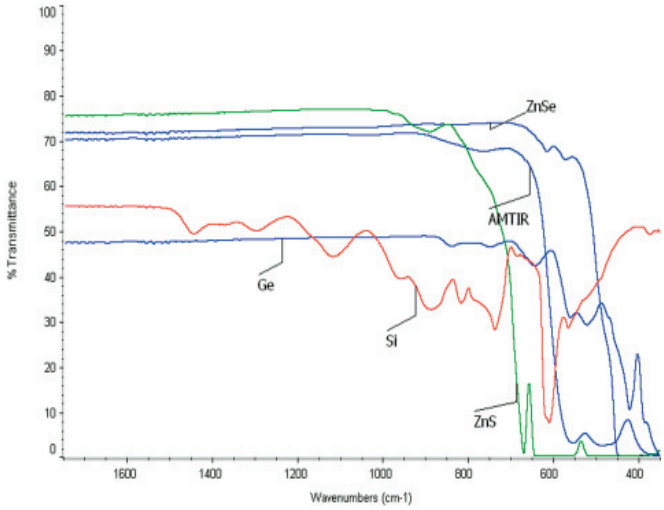

Figure 2. Transmission FTIR spectra for 2 mm thick windows of Ge, Si, ZnS, AMTIR and ZnSe.

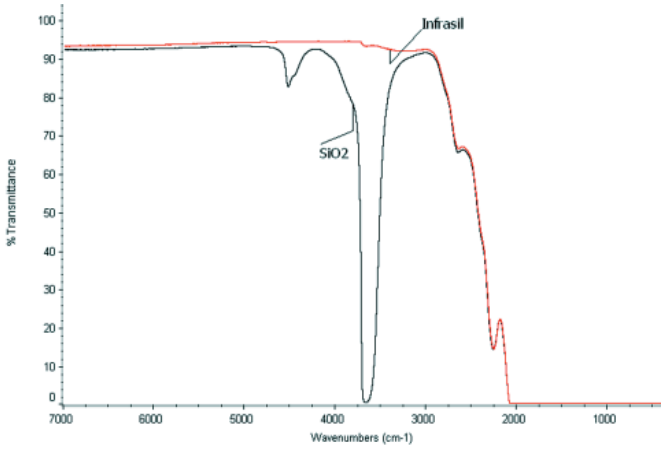

Figure 3. Transmission FTIR spectra for 2 mm thick windows of Infrasil (form of fused quartz) and SiO_2.

Set 3 of materials for IR transmission measurements include those materials which are not water soluble and have low refractive index (high transmissivity). These 2 materials are shown in Figure 3. As seen in these spectral data, Infrasil is essentially hydroxyl free SiO_2, and can be used in the mid-IR spectral region for hydrocarbon analysis. Use of SiO_2 in the mid-IR would have to be limited to a narrow spectra region about 3400 to 2600 cm-1 due to strong hydroxyl absorbance about 3675 cm-1.

Summary

A wide range of materials are available for liquid sampling in the mid-IR spectral region. The choice of window materials for your application can be made based upon the sample composition, aqueous content, pH, if applicable, and required spectral range for your analysis. Table 1 on page 3 summarizes the numerical values of these characteristics for the window materials in this review.

Table 1. Properties of Materials for Mid-IR Spectroscopy

Material	Comments	SWL, cm-1	LWL, cm-1	RI	Solubility	Hardness	MP	pH Range
AMTIR	SeAsGe glass, brittle	1100	593	2.5	0	170	370	1-9
BaF_2	Barium Fluoride	66600	691	1.45	0.17	82	1280	5-8
CaF_2	Calcium Fluoride	79500	896	1.4	0.0017	158	1360	5-8
CsI	Cesium Iodide, very hygroscopic, somewhat toxic	42000	172	1.73	44	20	621	NA
Ge	Germanium, brittle, becomes opaque at elevated temperature	5500	432	4.0	0	780	936	1-14
Infrasil	Silicon Dioxide (fused silica)	50000	2315	1.53	0	460	1713	1-14
KBr	Potassium Bromide, most widely used for mid-IR applications	48800	345	1.52	53	6	730	NA
KCl	Potassium Chloride	55600	385	1.45	35	7	776	NA
KRS-5	Thallium Bromide / Thallium Iodide, extremely toxic!	17900	204	2.37	0.05	40	414	5-8
NaCl	Sodium Chloride	52600	457	1.49	36	18	801	NA
SiO_2	Silicon Dioxide, strong IR absorbance at 3675 cm-1	50000	3735, 2315	1.53	0	460	1713	1-14
Si	Silicon, strong IR absorbance between 624-590 cm-1	8900	624, 30	3.41	0	1150	1420	1-12
ZnS	Zinc Sulfide	17000	690	2.2	0	240	1830	5-9

SWL – Shortest wavelength for transmission, 1 mm, 50% transmission
LWL – Longest wavelength for transmission, 1 mm, 50% transmission
RI – Refractive index, at relevant wavelength
MP – Melting point