Transmission Sampling Techniques – Theory and Applications

FTIR sampling by transmission is a very popular method for collection of infrared spectra. Its use is easy to explain – the methods are intuitive and do not require sophisticated sampling accessories. In many cases, the sample can be placed directly into the path of the infrared beam (with the help of sample holder) and scanned. Further benefits of transmission sampling techniques include compatibility with automated sampling and microsampling techniques such as IR Microscopy.

Transmission techniques are well documented and have been successfully used for many years. A large number of spectral libraries contain transmission spectra and are often used as references for the purpose of qualitative analysis. Transmission techniques offer many advantages and should be used whenever possible, unless reliable sample preparation becomes too difficult, too time consuming or impossible. Transmission is also widely used for quantitative applications, as significant numbers of basic measurements adhere to the Beer-Lambert law. The law provides a mathematical relationship between the infrared radiation absorbed by the sample and the sample concentration:

$$A = a \cdot b \cdot c$$

Where

- $A$ = absorbance
- $a$ = absorptivity
- $b$ = pathlength
- $c$ = sample concentration

The Beer-Lambert law states that absorbance is linearly proportional to sample concentration (with sample pathlength and absorptivity constant). The actual measurements are generated in percent transmittance (which is not a linear function of concentration); however, they can be converted in real time to absorbance by all modern FTIR software packages. As mentioned before, transmission measurements are intuitive and simple. Many samples are too thick to be measured directly and they have to be processed in some way before meaningful data can be collected. Some of the sample preparation techniques are time consuming and can be destructive. Liquids and pastes are generally the easiest samples to run. A large number of liquid cells and windows are available for liquid measurements. Solid samples (with the exception of thin films) require sample preparation – making a pellet (typically potassium bromide – KBr) or a mull. Gas samples require a suitable gas cell with a pathlength sufficient to detect the desired component.

Sample Preparation and Analysis

Liquids

Most liquids and dissolved solids are easy to measure by transmission. Viscous liquids or pastes can be simply pressed between two IR transparent windows and measured by FTIR.

Thin liquids or samples in solvent may be best run by using a demountable liquid cell or a sealed cell, consisting of two windows with a precision spacer in-between. One of the windows has two drilled holes for the introduction and evacuation of the sample. A large number of cell options are available – these include permanently sealed cells and demountable cells with different window materials and a wide selection of spacers.

The pathlength of liquid cells can be easily measured with your FTIR spectrometer. Just place the empty cell into the FTIR and collect its spectrum. The frequency of the sine wave spectrum (produced by back reflection within the cell) provides the pathlength using the following equation:

$$P = (10 \cdot N) / (2 \cdot \Delta \text{ cm}^{-1})$$

Where

- $P$ = pathlength of cell in mm
- $N$ = number of fringes within $\Delta \text{ cm}^{-1}$
- $\Delta \text{ cm}^{-1}$ = wavenumber difference of fringe count

It is very important to select compatible IR transparent windows for your liquid samples. Please refer to the table on the last page of this note to select your windows. If you still have questions, please call us.

FTIR spectrum of 1 drop of extra virgin olive oil pressed between 25-mm KBr windows and held in the IR beam using the PIKE Universal Sample Holder.
**Solids**

The easiest to analyze are film and polymer samples less than 200 micrometers thick (ideal thickness for the major component of a polymer film is about 20 microns). These samples can be simply placed into a sample holder and immediately scanned.

The thickness of the polymer film can be calculated from the fringe pattern in the spectrum using the following equation:

\[ T = \left( \frac{10000 \cdot N}{2 \cdot n \cdot \Delta \text{cm}^{-1}} \right) \]

Where

- \( T \) = thickness of polymer film in microns
- \( N \) = number of fringes within \( \Delta \text{cm}^{-1} \)
- \( \Delta \text{cm}^{-1} \) = wavenumber difference of fringe count
- \( n \) = refractive index of polymer

The same procedure can be used for samples which can be sliced and pressed to an appropriate thickness – especially for IR microsampling. PIKE Technologies’ Heated Platens Accessory is ideal for making thin polymer films.

For IR microsampling, one can place a small sliced sample into a sample compression cell and apply pressure to hold the sample and to thin it to a usable thickness – as shown in the following spectral data.

However, the majority of solid materials must be prepared before their infrared spectra can be collected. In many cases sample preparation involves grinding of the sample and mixing it with an IR transparent material such as KBr and then pressing a pellet. While this method of solids analysis is time consuming, it produces an excellent result.

**Solid Sample Preparation Tips**

The best method for preparation of solid samples involves mixing the sample (about 5% by weight) with an IR transparent material (typically KBr) and pressing a pellet. The mixing is best done with the ShakIR accessory which produces a fully mixed and pulverized sample in about 20 seconds. The grinding and mixing can also be done with a mortar and pestle – but not as well. Generation of a pellet involves pressing the prepared mixture with a hydraulic or hand press into a hard disk. The pellet, ideally 0.5 to 1 mm thick is then placed in a transmission holder and scanned. Typically, the pellet technique provides good quality spectra with a wide spectral range and no interfering absorbance bands.

Samples which do not grind well and/or are affected by solvents and mulling agents can be analyzed with high-pressure techniques. Typical samples include fibers and paint chips. The accessory used for such applications utilizes two diamond anvils. Difficult samples are placed between the diamonds and crushed, compressed and flattened to the thickness necessary to obtain good-quality FTIR spectra. Diamond cells are transparent to IR radiation except in the region of 2400 cm\(^{-1}\) to 1700 cm\(^{-1}\). The high-pressure diamond cells require the use of a beam condenser or an infrared microscope.

An alternate method for analysis of solid materials involves making a mull. Mulls are sample suspensions in Nujol (refined mineral oil) or Fluorolube (perfluorohydrocarbon). The process is based upon mixing 1 to 2 drops of the mulling agent with a ground sample until a uniform paste is formed. The paste is transferred onto a KBr or other IR transparent disk, placed in the sample compartment of the spectrometer and scanned. The advantage of this technique is that it is a relatively quick and simple procedure; disadvantages include interference from mulling agent absorption bands. Both Nujol and Fluorolube have characteristic spectral features and in most cases have to be used as a pair in order to generate a complete mid IR spectrum. Nujol is used below 1330 cm\(^{-1}\), Fluorolube above 1330 cm\(^{-1}\). Some sample preparation is needed and the quality of the results and amenability to automation and microsampling offer significant advantages.
Gases
Analysis of gas samples is a unique form of transmission sampling by FTIR as the identified sample does not need to be of pure composition. At high spectral resolution, most gas mixtures can be identified and quantified since absorbance bands can be selected within the spectrum, which are resolved and distinct from other components within the sample.

Simple demountable cells (50 mm to 100 mm) are recommended for samples in a 1–10% by weight concentration range.

For highly dilute samples (ppm to ppb concentrations), long-path cells are required. The long-path cell reflects the IR beam several times through the sample using a set of mirrors positioned on the opposite ends of the cell, producing a pathlength from 2.4 to 30 meters – or more. It is important to select window materials compatible with the investigated sample. Gas sampling accessories can be fitted with different windows to accommodate the physical and chemical characteristics of the measured gas. Some gas measurement applications require temperature control for higher precision or to prevent condensation of specific components. Special designs for high-pressure and temperature controlled experiments are also available.

Properties of Select Infrared Transmitting Materials For Transmission Spectroscopy

<table>
<thead>
<tr>
<th>Material</th>
<th>Comments</th>
<th>SWL cm⁻¹</th>
<th>LWL cm⁻¹</th>
<th>RI</th>
<th>Solubility g/100 g</th>
<th>Hardness kgf/mm²</th>
<th>MP °C</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMTIR</td>
<td>GeAsSe glass, brittle</td>
<td>11000</td>
<td>593</td>
<td>2.50</td>
<td>0.00</td>
<td>170</td>
<td>370</td>
<td>1–9</td>
</tr>
<tr>
<td>BaF₂</td>
<td>Barium Fluoride</td>
<td>66600</td>
<td>691</td>
<td>1.45</td>
<td>0.17</td>
<td>82</td>
<td>1280</td>
<td>5–8</td>
</tr>
<tr>
<td>CaF₂</td>
<td>Calcium Fluoride</td>
<td>79500</td>
<td>896</td>
<td>1.40</td>
<td>0.0017</td>
<td>158</td>
<td>1360</td>
<td>5–8</td>
</tr>
<tr>
<td>CsI</td>
<td>Cesium Iodide, very hygroscopic, Somewhat Toxic</td>
<td>42000</td>
<td>172</td>
<td>1.73</td>
<td>44</td>
<td>20</td>
<td>621</td>
<td>NA</td>
</tr>
<tr>
<td>Diamond</td>
<td>Type Ila, strong IR absorbance between 2700–1800 cm⁻¹, costly</td>
<td>30000</td>
<td>&lt;2</td>
<td>2.40</td>
<td>0.00</td>
<td>5700</td>
<td>550</td>
<td>1–14</td>
</tr>
<tr>
<td>Ge</td>
<td>Germanium, brittle, becomes opaque at elevated temperatures</td>
<td>5500</td>
<td>432</td>
<td>4.00</td>
<td>0.00</td>
<td>780</td>
<td>936</td>
<td>1–14</td>
</tr>
<tr>
<td>KBr</td>
<td>Potassium Bromide, most widely used for mid-IR applications</td>
<td>48800</td>
<td>345</td>
<td>1.52</td>
<td>53</td>
<td>6</td>
<td>730</td>
<td>NA</td>
</tr>
<tr>
<td>KRS-5</td>
<td>Thallium Bromide/Thallium Iodide, Extremely Toxic!</td>
<td>17900</td>
<td>204</td>
<td>2.37</td>
<td>0.05</td>
<td>40</td>
<td>414</td>
<td>5–8</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
<td>52600</td>
<td>457</td>
<td>1.49</td>
<td>36</td>
<td>18</td>
<td>801</td>
<td>NA</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>For Far-IR, swells with some organic solvents</td>
<td>625</td>
<td>&lt;4</td>
<td>1.52</td>
<td>0.00</td>
<td>110</td>
<td>1.5–14</td>
<td>NA</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon Dioxide</td>
<td>50000</td>
<td>2315</td>
<td>1.53</td>
<td>0.00</td>
<td>460</td>
<td>1713</td>
<td>1–14</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon, strong IR absorbance between 624–590 cm⁻¹</td>
<td>8900</td>
<td>624, 30</td>
<td>3.41</td>
<td>0.00</td>
<td>1150</td>
<td>1420</td>
<td>1–12</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zinc Sulfide</td>
<td>17000</td>
<td>690</td>
<td>2.20</td>
<td>0.00</td>
<td>240</td>
<td>1830</td>
<td>5–9</td>
</tr>
<tr>
<td>ZnSe</td>
<td>Zinc Selenide</td>
<td>15000</td>
<td>461</td>
<td>2.40</td>
<td>0.00</td>
<td>120</td>
<td>1526</td>
<td>5–9</td>
</tr>
</tbody>
</table>

Notes: The above table is meant to be a general guide – brief and concise. For more information about these materials, consult appropriate reference books and Safety Data Sheets (SDS).

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