TECHNICAL NOTE

FT-IR Spectrometry

Obtaining Optimum Reproducibility for FT-IR Measurements in ZnSe Liquid Transmission Cells

Introduction

Zinc selenide is a very useful material for infrared sampling optics, since it is transparent over most of the mid-infrared range, fairly hard and durable, and resistant to water and most chemicals. Consequently, it is widely used for attenuated total reflectance (ATR) and liquid transmission cells. Its relatively high refractive index of 2.4 is useful for ATR, but for transmission measurements, it can lead to several artifacts, the character and severity of which can vary between cells. This note describes these artifacts and the steps that can be taken to effectively eliminate them, ensuring equivalent results across systems and cells.

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Artifacts caused by ZnSe windows

Interference fringes

Interference fringes are commonly used to determine the pathlength of liquid cells – when the cell is empty, prominent fringes are observed in the spectra, as light is reflected multiple times between the parallel internal faces of the cell and undergoes constructive or destructive interference, depending on the ratio between the pathlength and the wavelength of the light. As the wavelength axis spacing of an FT-IR spectrum is very precisely known, measurement of the fringe spacing allows a precise determination of the cell pathlength.

With window materials, such as KBr that have refractive indices similar to that of organic liquids (see Table 1), the reflections within the cell are very much reduced when the cell is filled and the magnitude of the interference fringes is dramatically reduced. With ZnSe, however, this is not the case, and appreciable fringes are seen even when the cell is filled.

Table 1. Approximate refractive indices in the mid-infrared for some common window materials and organic liquids.

Material	Refractive index at 2 µm
Zinc selenide	2.4
Potassium bromide	1.5
Heptane	1.3
Benzene	1.45
Mineral oils	1.3–1.4

These interference fringes can affect both qualitative and quantitative interpretation of spectra, so it is desirable to eliminate or mitigate them where possible. Interference fringes can be reduced by a number of methods – either computationally, by removing the appropriate frequency component during the Fourier transform processing; or optically, by holding the cell at Brewster's angle to the beam, employing curved windows, or breaking the parallelism of the windows by means of a wedged spacer.

The latter approach is employed in the PerkinElmer Frontier™ OilExpress oil condition monitoring system. Interference fringes for an empty cell (the worst-case scenario) are typically <0.002 A at 2000 cm^{-1}, and optical calculations and experimental results indicate that a reduction by at least a factor of three can be expected when the cell is filled with an organic liquid.

Figure 1 shows the spectrum of a wedged ZnSe flow cell. The interference fringes are well-controlled (note the expanded ordinate scale), although clearly visible above the noise.

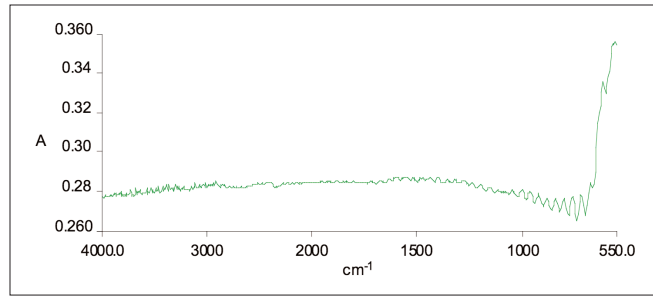

Figure 1. Spectrum of an empty ZnSe flow cell with a wedged 0.1 mm spacer.

Baseline offsets with empty and filled cells

A second effect that ZnSe windows have on transmission spectra is to introduce a baseline offset due to reflectance losses. This is illustrated schematically in Figure 2, and shown experimentally in Figure 3. The transmittance of an empty cell is about 47%, corresponding to an absorbance offset of about 0.32. When the cell is filled, the transmittance of the interfaces increases to 60%, corresponding to an absorbance offset of 0.22.

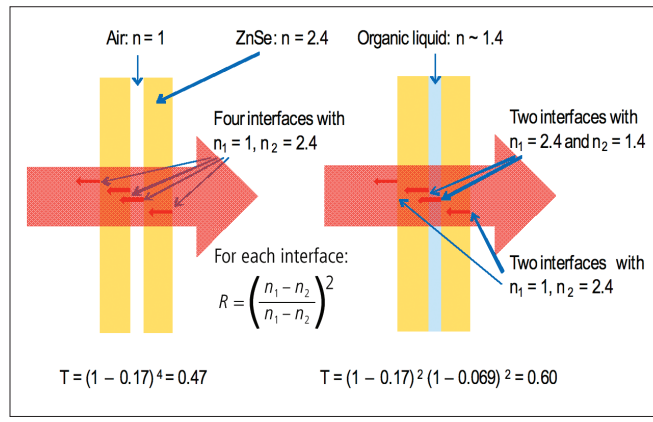

Figure 2. Schematic illustrating the difference in reflection losses between empty and filled ZnSe cells. In a region where the sample is transparent, the transmittance of the cell, T, can be estimated as the product of the transmittances of the four interfaces. An accurate calculation takes into account all the multiply-reflected rays as well.

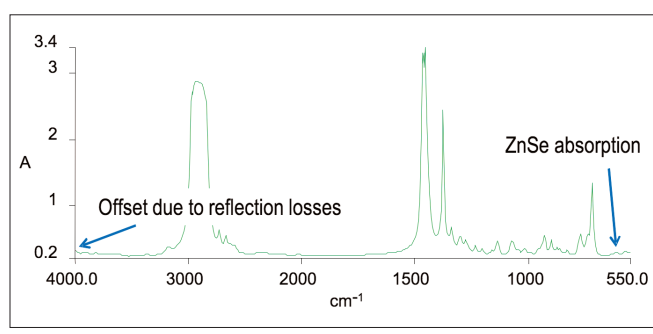

Figure 3. Spectrum of heptane in a ZnSe flow cell with a wedged 0.1 mm spacer.

Correcting ZnSe cell artifacts

Subtracting an empty-cell spectrum

Since the precise extent of the reflection losses can vary from cell to cell, it is desirable to correct spectra for this artifact to ensure maximum reproducibility between systems. The most obvious tactic is simply to measure the empty-cell spectrum and subtract this from the sample spectrum, as shown in Figure 4. This approach does correct the shape of the baseline, but has two drawbacks. First, since the magnitude of the residual interference fringes is greater in the empty-cell spectrum than in the sample spectrum, subtracting the empty-cell spectrum actually has the effect of worsening the interference fringes in the sample spectrum. If the fringes in the empty-cell spectrum are sufficiently small this may not be a significant issue. The second problem is that a negative offset will be introduced to the spectrum. The reason for this is that the reflection losses for the filled cell are lower (see Figure 2).

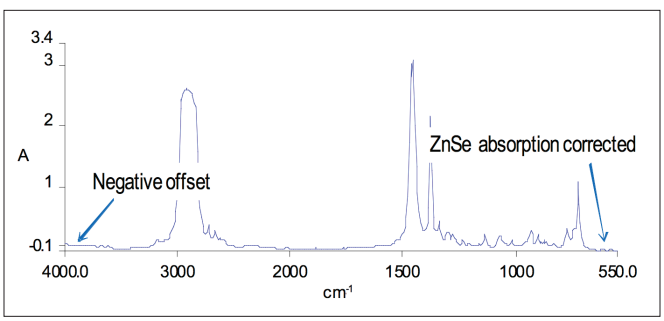

Figure 4. Spectrum of heptane minus the spectrum of the empty cell.

Subtracting a modified empty-cell spectrum

Both of these issues can be addressed by modifying the empty-cell spectrum prior to subtracting it from the sample spectrum. Since the spectral features (except for the interference fringes) in the empty-cell spectrum are very broad, a smoothing window can be chosen such that the interference fringes will be smoothed away but the baseline shape will not be appreciably affected. In the present example, a width of 100 points with the Interactive Smooth function in Spectrum software was found to be ideal.

The negative offset can be predicted by some simple reflectance calculations, as shown in Figure 2. We calculate the expected transmittance of the empty cell and then of the filled cell, assuming a refractive index of 1.4 for the sample. Most organic liquids have a refractive index between 1.3 and 1.6, and within this range the difference in reflection losses is very close to 0.067 absorbance units.

This approach has both the advantages of considering the variation between individual cells in terms of reflection and absorption losses, and of obtaining spectra with a baseline as near to zero as possible (or, in the case of samples with a "genuine" baseline, such as sooty oils, with a baseline as near to the real value as possible). The effectiveness of this procedure is indicated in Figure 5, which shows the heptane spectrum corrected by subtracting an empty-cell spectrum modified as described above.

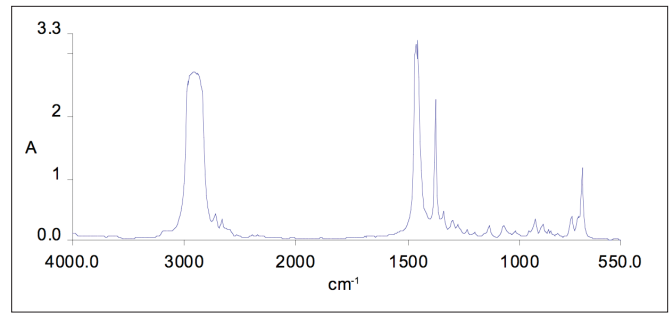

Figure 5. Spectrum of heptane minus the corrected empty-cell spectrum.

Pathlength considerations

In addition to correcting for artifacts introduced by the ZnSe cell, for quantitative measurements it is also necessary to know precisely the pathlength of the cell. There are two general approaches for making this measurement, each with its benefits and drawbacks.

Measurement via interference fringes

Traditionally, the pathlength of an infrared liquid cell is determined by measuring the spectrum of the empty cell, determining the distance on the abscissa scale between the peaks or troughs of n fringes (typically n > 10) and using the following equation:

$$d = \frac{10n}{2(\nu_2 - \nu_1)}$$

where d is the pathlength in mm and ν_1 and ν_2 are the positions of the fringe extrema in cm^{-1}.

However, this approach becomes difficult when the interference fringes are well-suppressed, as with the OilExpress flow cells. One strategy to increase the magnitude of the interference fringes is to use the instrument's internal J-stop aperture to reduce the illuminated area of the sample. This reduces the effectiveness of the wedging and allows the pathlength to be determined. However, it must be considered that, since only a small area of the cell is actually being measured, greater reliance is being placed on the flatness of the window faces and the centrality of the beam within the cell aperture.

Measurement via an absorbance standard

An attractive alternative to the use of interference fringes is to measure the absorbance of a standard material in the cell and use a comparison of this against tabulated or previously measured spectra to derive a value for the effective cell pathlength.

This method relies on the existence of a stable, reliable absorbance standard. In principle, any liquid with a suitable absorption band can be used. In the OilExpress system, the heptane cell-flush solvent is used as a standard. It is important to ensure that high-purity heptane is used, and that the temperature of the standard is always the same as during the reference measurement, so that changes in density do not affect the result.

While it is easy to establish precise relative differences between cells and systems with this approach, obtaining an absolute value for the pathlength is less straightforward, since it requires an accurately known absorptivity value for the standard. A further complicating factor with high refractive index windows is the contribution to the absorption from rays that pass through the sample multiple times, having been reflected from the windows. This effect is on the order of 10% for weak bands.

Implementation in Spectrum and OilExpress software

	Spectrum version 6	Spectrum version 10
1	Clean and dry the flow cell; measure the empty-cell spectrum using the same scan settings as OilExpress.	
2	Use the Interactive Smooth function to remove any interference fringes (a filter width of about 100 should be appropriate).	Use the Smooth process to remove any interference fringes (a filter width of about 100 should be appropriate).
3	Use the Spectral Calculator to subtract 0.067 from the absorbance-mode spectrum.	Use the Arithmetic process to subtract 0.067 from the absorbance-mode spectrum.
4	Save the spectrum, and import it into OilExpress software using the Reference Spectrum Manager (be sure to enter the correct pathlength when prompted).	
5	Use this modified empty-cell spectrum as the reference spectrum for absolute methods such as JOAP and ASTM® E2412 Direct Trending.	

An empty cell correction tool is supplied with OilExpress 4 systems, steps above are not required.

The absorptivity values used by the OilExpress system were obtained by numerous measurements of heptane in liquid cells with pathlengths precisely determined by the interference-fringe method.

Results and discussion

Empty-cell spectra were measured for three OilExpress flow cells, smoothed and corrected as described above, and used to correct the spectra of a used-oil sample measured in the three cells. The cell pathlengths were determined by measuring spectra of heptane, and the sample spectra were normalized to a pathlength of 0.1 mm. The corrected oil spectra along with calculated results for two analytes (soot and phenolic antioxidant) are shown below in Figure 6. The spectra are almost indistinguishable, and the relative standard deviations for the analytes are under 2% in both cases.

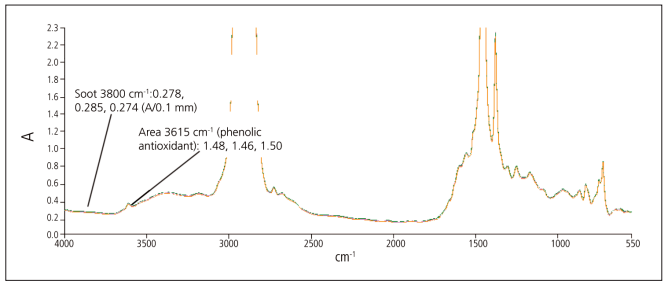

Figure 6. Spectra of a diesel engine oil measured in three flow cells following empty-cell correction and pathlength normalization. Calculated results for soot and phenolic antioxidant are shown.

Conclusions

ZnSe is a very useful material for liquid cells in the infrared, but it requires some care to ensure the best reproducibility of results between cells. This note has described an approach to interference fringes, reflection losses and pathlength variations that deals effectively with the variability between cells and ensures the best possible results for quantitative analyses.

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