

Improved Measurement of Liquid Samples Using FTIR

Cary 630 FTIR spectrometer with DialPath module offers benefits over ATR measurements.



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Introduction

Ensuring the quality of incoming raw materials as well as finished products in the material, cosmetics, chemicals, pharmaceutical and other manufacturing industries is crucial, and FTIR spectroscopy is widely used for this purpose. When these materials are liquids, the analyst currently has two choices for analysis methodology—transmission spectroscopy or attenuated total reflectance (ATR) spectroscopy.

Prior to 1980, only the transmission method was widely used for the analysis of liquids by mid-IR spectroscopy. Transmission cells were classified as two types: sealed or variable pathlength. Sealed cells were factory-set at a fixed pathlength and constructed with window materials appropriate for the application. Liquid samples were introduced into sealed cells by syringes and Luer-Lock type fittings. These cells were acceptable for less viscous liquids, but suffered from filling and cleaning problems when more viscous liquids were measured.

Variable pathlength cells featured demountable windows that allowed the operator to adjust the pathlength required for a specific application by using pre-cut spacers, typically made of PTFE. These cells offered more flexibility than the fixed pathlength cells, but suffered from leakage and problems with fringing that would affect the performance.

After 1980, ATR-type liquid cells began to appear in significant numbers. Because these devices tended to be far easier to use, their popularity increased to the point where ATR today (for both solids and liquids) is the most widely used sampling technique for mid-IR spectroscopy. For ATR, the pathlength of measurement is defined by the depth of penetration of the evanescent wave, which is wavelength dependent, multiplied by the number of reflections. Thus, the maximum pathlength that can be achieved by the typical ATR element material (diamond or ZnSe) is typically not more than about 12 to 15 μm . ATR is quite effective for shorter pathlength measurements (neat liquids or mid-IR opaque solutions with higher-concentration analytes), whereas for longer pathlength mid-IR measurements, transmission spectroscopy employing the fixed or variable pathlength cells described above is still the standard.

DialPath—changing how liquids are analyzed by FTIR

The Agilent DialPath technology is an innovative way to measure liquids. DialPath offers the variable pathlength capability of classic transmission cells with the ease of use and simplicity of the ATR method. The technology (Figure 1) features an optical head that can be rotated to select one of three factory-calibrated, fixed pathlengths between 30 and 1000 μm . To analyze a sample, a small drop of liquid sample is placed between two horizontally positioned windows of the DialPath module, as shown in Figure 1 and Figure 2 (middle). The liquid is sandwiched between the two windows and the distance between the two windows defines the highly reproducible optical pathlength. For lower-concentration samples, one of the longer pathlength window sets is selected; for samples that are more concentrated, a shorter pathlength combination is used. The two windows can be wiped clean, preparing the device for the next sample.

The Agilent Tumbler module, which uses the same technology as the DialPath module, has one pathlength available rather than three. Both modules are permanently aligned and are easily attached to the front of the Cary 630 FTIR engine (Figure 3).

The analyzer has many advantages over the older transmission cell technology:

- It permits instantaneous selection of three different pathlengths as needed
- No disassembly is required to change pathlengths
- No spacers are required—cell leakage and fringing are eliminated
- No autosampler is needed to introduce samples
- Liquids of varying viscosity can be handled equally effectively
- Volatile solutes and solvents are accurately measured
- Sample cleanup is very quick
- Samples can be analyzed rapidly
- No supplies or consumables (cell windows, spacers, cleaning solvents, and so forth) are required

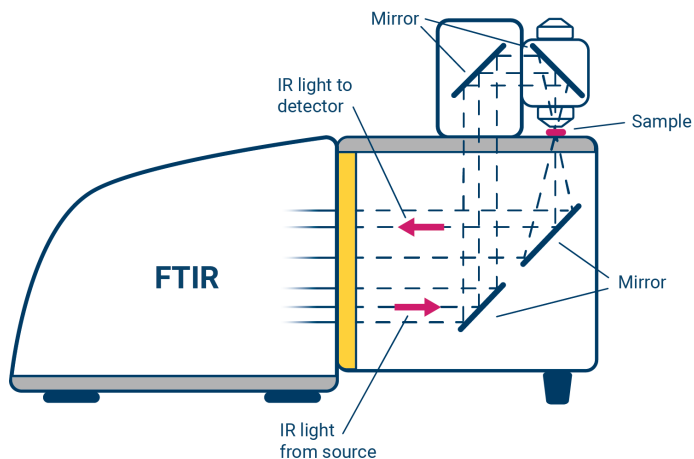


Figure 1. An optical diagram of the light path through the DialPath module and the Cary 630 FTIR spectrometer.



Figure 3. Agilent Cary 630 FTIR spectrometer equipped with the Agilent-exclusive DialPath sampling module. The Cary 630 is an ultra-compact, easy to use, high performance FTIR spectroscopy. Combined with DialPath technology, it is a powerful instrument for the analysis of liquids.

Experimental and results

Liquid propylene glycol, glycerol, triacetin, and dipropylene glycol are used as additives in foods, drugs, and cosmetics. These additives were analyzed using DialPath technology to verify their identity and overall purity. In order to obtain high-quality mid-IR spectra, the short, 30 μm pathlength was selected to ensure that the absorbance of the sample was within the measurement range of the instrument. The spectra (Figure 4), consisting of 64 co-added interferograms at 4 cm^{-1} resolution, took approximately 30 seconds to collect. These spectra were then compared to reference spectra contained in an on-board library, which yielded a match quality of better than 0.99 for each (scale of 0 to 1.000, with 1.000 being a perfect match). The quality of the match confirms the gross identity and purity of the four liquids.

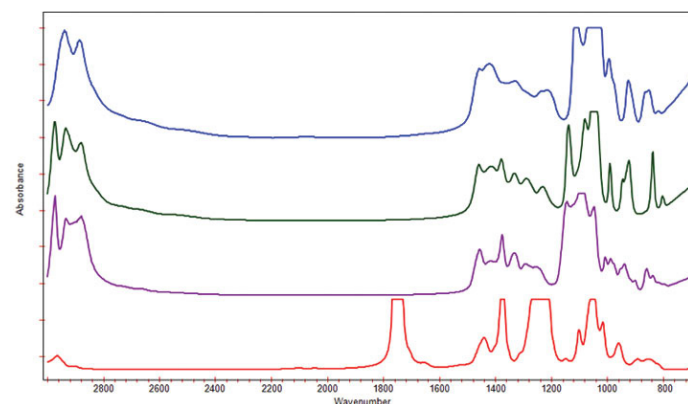


Figure 4. Spectrum of product compounds recorded using the DialPath 30 μm pathlength. Blue = glycerol, red = triacetin, green = propylene glycol and purple = dipropylene glycol.

Figure 2. Liquid sample analysis. Three steps to analysis with the DialPath module.

Present in these product compounds are low-level impurities that must be measured, since there is a specific threshold value that cannot be exceeded for human use. Neat samples of the two major impurities, ethylene glycol and diethylene glycol, were measured using the 30 μm pathlength window set. The spectrum of each impurity is similar to one another (Figure 5) and also to that of the pure compounds. In order to determine the level of these impurities, a series of calibration samples were made up that varied the amount of both impurities in each of the individual compounds. The infrared absorbance of the impurity bands will increase proportionately to concentration, as Beer's Law states. Separate calibrations were developed using a partial least squares (PLS) algorithm for each of the impurities in the compounds. The PLS chemometrics allows for accurate modeling of the molar absorptivity of the ethylene glycol and diethylene glycol absorbance bands of interest in each of the additives.

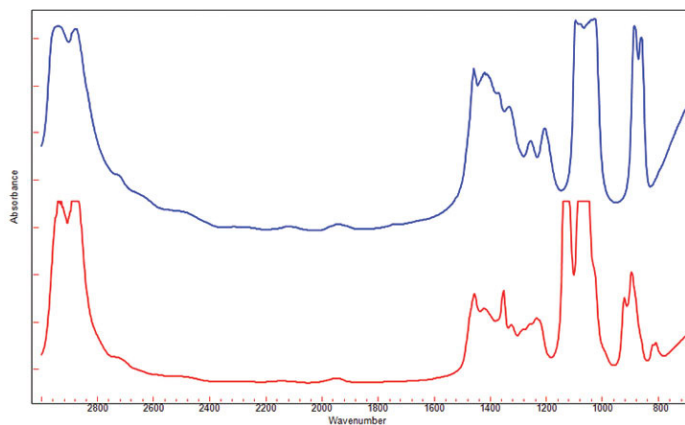


Figure 5. Spectra of ethylene glycol (blue) and diethylene glycol (red) impurities recorded using the 30 μm pathlength. Spectra are similar to each other and to the spectra of the product compounds.

Because the spectra of the impurities and additives are so similar, specific wavelength regions were used for the measurement. For example, in the case of glycerol, the spectral regions from 875 to 905 cm^{-1} and 1130 to 1200 cm^{-1} were found to be effective for measuring the impurity bands. However, the 100 μm pathlength was found to be too long, obscuring the bands of interest (Figure 6), and the 30 μm pathlength did not provide the level of sensitivity required to measure the impurities. For this reason, the 75 μm pathlength was selected to carry out the analysis.

The latter pathlength provides enough transparency in the region of interest, and also provides adequate pathlength to measure the impurities. PLS-based calibrations for the impurities in glycerol (Figure 7) were found to have R^2 of 0.9895 for ethylene glycol and 0.9745 for diethylene glycol. Based on these calibrations, limits of quantitation (LOQ) of approximately 0.075 vol% and limits of detection (LOD) of 0.04 vol% were obtained for both impurities in glycerol. Since the limit of quantitation is well below the FDA limit of 0.1 vol%, the user can be confident that the glycerol is clean, and the much lower LOD gives the user the ability to optimize the production process to minimize the contaminants in these compounds. The Agilent MicroLab software automatically performs all calculations directly after data acquisition and presents the final results in an easy to understand format. The method development chemist can set thresholds for color-coding of the results and define if actions are recommended based on the result (Figure 8).

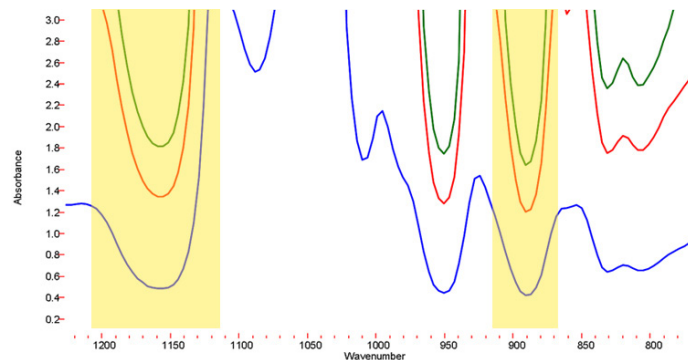


Figure 6. For glycerol, the 100 μm pathlength (green) is too opaque and the 30 μm pathlength (blue) does not provide an adequate limit of detection for the impurities. The 75 μm (red) pathlength provides the necessary sensitivity to detect impurity levels. The yellow panels indicate the spectral regions found to be effective for measuring impurity bands.

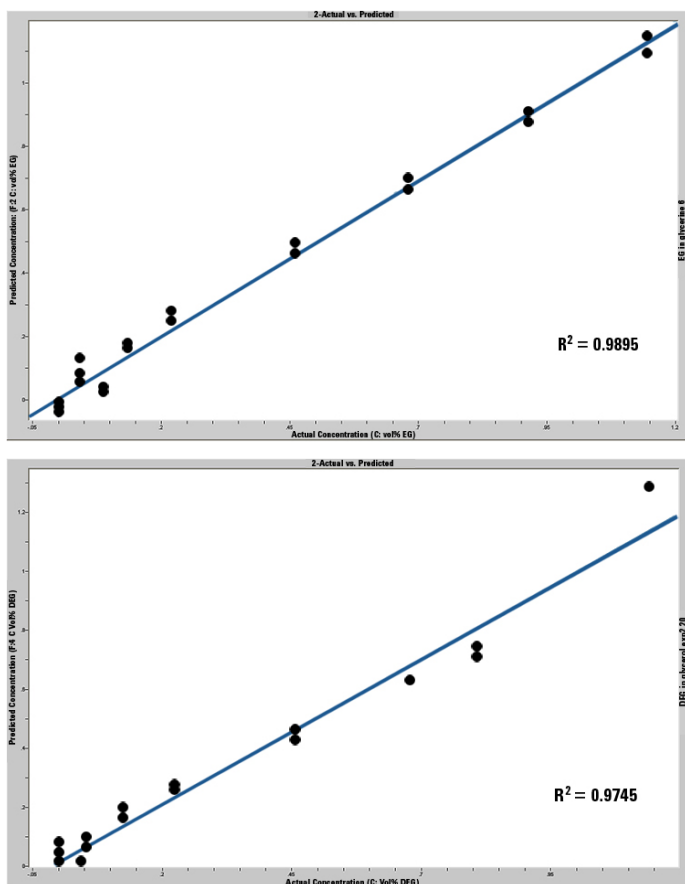


Figure 7. Calibration plots of ethylene glycol (top) and diethylene glycol in glycerol (bottom). Calibration plot of impurities in glycerol shows very good R^2 values and limits of detection of 0.04 vol% for each.

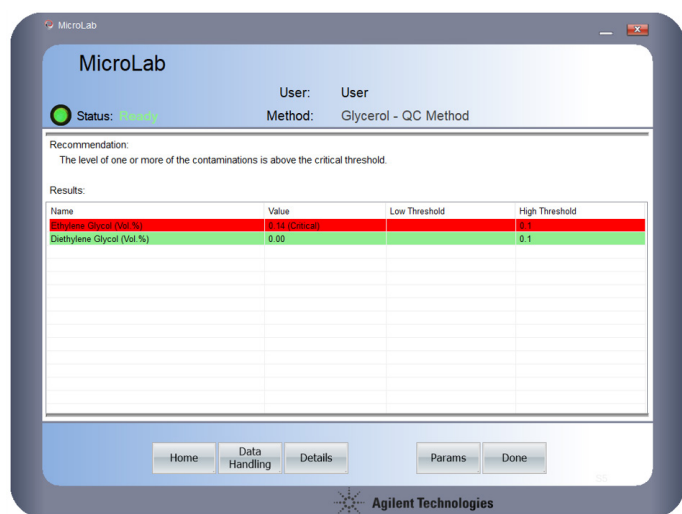


Figure 8. The Agilent MicroLab software displays analysis results for the level of ethylene glycol impurity in glycerol. Color-coded, actionable results are reported directly after data acquisition in line with the threshold settings of the method. The red color band shows that the level of impurity is outside of specification.

The measurement of impurities in glycerol is an excellent example of the importance of being able to select the correct pathlength to achieve optimum sensitivity in a critical measurement. Because of the viscosity of glycerol, the analyst might choose an ATR method for the measurement, since traditional transmission liquid cells are difficult to fill with viscous liquids. The ATR method would result in a very good quality spectrum of the neat glycerol, but, because of its limited pathlength, the method would not provide the levels of quantitation of the impurities that the 75 μm pathlength achieves. Yet, the DialPath technology is as easy to use as an ATR cell, both for sample introduction and sample cleanup.

Similar procedures were carried out for the detection of the ethylene glycol and diethylene glycol impurities in the triacetin, propylene glycol, and dipropylene glycol additives. As an example, for the detection of these impurities in triacetin, it was found that the 100 μm pathlength provided the optimum results. This is because triacetin has relatively transparent regions in its spectrum between 812 and 939 cm^{-1} and 1100 and 1200 cm^{-1} (as shown in Figure 4), which are well suited for detecting the impurity bands. Triacetin is even less optically opaque in this region than in the previous example of glycerol, enabling the use of the longer pathlength. Calibration of the impurities in triacetin via PLS yielded R^2 values for ethylene glycol and diethylene glycol of 0.9997 and 0.9998, respectively, with limits of detection of 0.04 vol% for ethylene glycol and 0.02 vol% for diethylene glycol. Measurement of triacetin samples using these calibrations indicates that the levels of impurities are within the correct specification range; however, diethylene glycol is detected at low levels (0.04% or 400 ppm), which may warrant closer attention.

Conclusion

Overall simplicity is the main reason ATR analysis of neat liquids and/or of higher-concentration analytes has become popular. ATR, however, offers limited pathlength choices and is not effective when measuring lower concentration analytes. This is well illustrated in the examples in this study, which aimed to quantitate low-level impurities, with spectra similar to those of the desired products, in order to ensure that the incoming additives were within manufacturing specification.

In this example, transmission measurements were necessary to achieve the limits of quantitation required, but doing so with traditional liquid transmission cells is cumbersome and potentially less accurate, particularly for liquids as viscous as glycerol.

The Cary 630 FTIR with DialPath module allows the user to quickly and accurately select the correct longer pathlength needed for detecting lower-level analytes, and provides the ability to choose a shorter pathlength for use in gross identification of liquids. At the same time, the DialPath technology enables these measurements to be carried out as easily and quickly as ATR for the shorter pathlength situations. In fact, DialPath technology obviates the need to use ATR for the measurement of many neat liquids to verify identity, since it is just as fast and easy to use as ATR.

www.agilent.com/chem/cary630

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