FTIR transmission measurement of volatile liquids using the Cary 630 FTIR equipped with DialPath technology

Application note

Specialty chemicals

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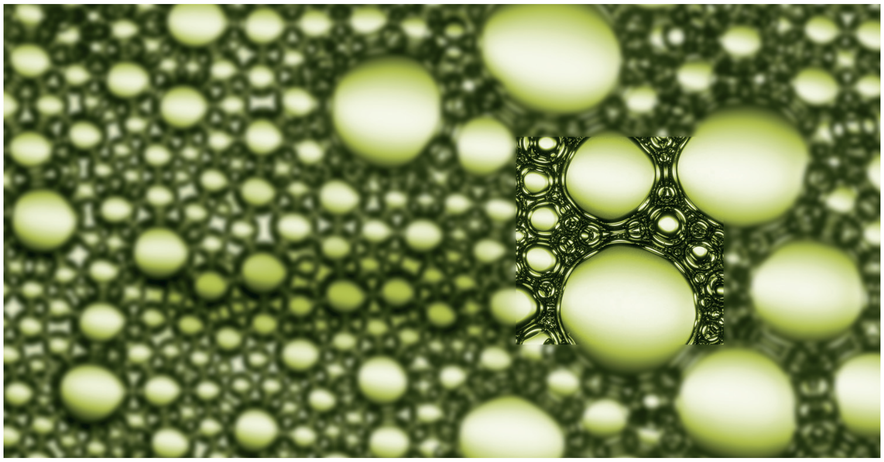

Introduction

Agilent's new DialPath technology, featured on the Cary 630 FTIR spectrometer (Figure 1a), is the first major breakthrough in FTIR transmission measurements of liquids in decades. The DialPath technology makes longer pathlength transmission measurements as easy and quick as ATR makes short pathlength liquid analysis. This sampling accessory has three individual pathlengths that can be accessed in seconds, and is a significant new sampling methodology that simplifies both quantitative and qualitative analysis.

Traditionally, the quantitative analysis of liquids by FTIR spectroscopy requires a sealed fixed pathlength cell. This technique is widely used for quantitative analysis of analytes in volatile solvents with applications in the fuel, chemical, and pharmaceutical industries. Use of sealed cells requires a skilled user to add the sample to the cell by syringe, taking great care to avoid air bubbles or incomplete filling of the cell. Improper filling can also cause damage to sealed cells by breaking the window or amalgam seal with

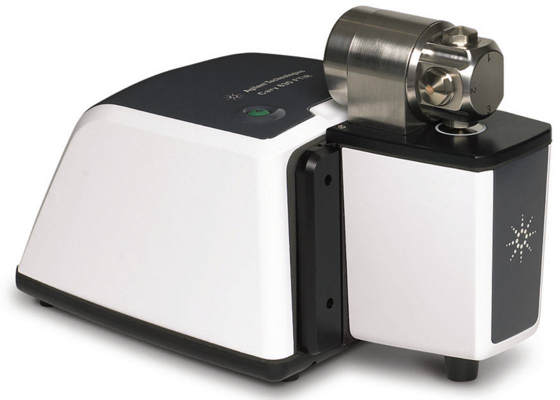

Figure 1a. The Cary 630 FTIR spectrometer fitted with DialPath accessory. The user simply places a drop of the liquid on the stationary window and then rotates a second window into place, thus creating a fixed pathlength.

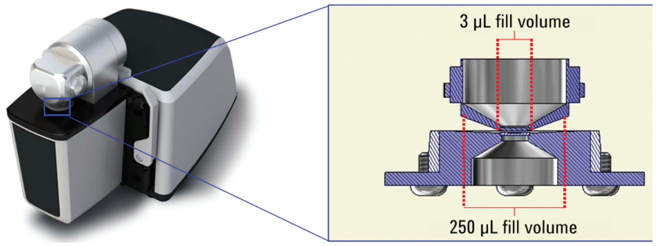

Figure 1b. The expanded sample interface region of one of the cells (right). The relatively small 'active region' (3 µL fill volume) in proportion to the total filled cell volume minimizes the effects of evaporation and diffusion in the < 60 s time scale.

excess pressure. These cells are also prone to internal reflections that cause significant spectral artifacts called 'fringing' and baseline noise features from improper cell placement into the spectrometer.

One of the major characteristics of DialPath accessory is that it features an 'open cell' design. There are no seals, spacers, syringes, or fragile window assemblies as in classical transmission spectroscopy. This makes the technology substantially easier to use for non-volatile and viscous liquids, where filling and cleaning is problematic. An obvious question arises on the measurement of samples or solutes that are volatile. How does an open cell (non-sealed) design handle the problem of sample evaporation and its concurrent effect on quantitative measurements?

The combination of the design of the DialPath technology and the performance envelope of the Cary 630 FTIR makes the analysis of highly volatile solvents and solutes straightforward.

- The DialPath open cell has an 'active region' (the area actually scanned by the infrared beam) that requires just 3 microliters of a liquid to make a reliable measurement (Figure 1b). The total fill volume of the DialPath cell is approximately 250 microliters. Thus, the small active region is quite small in proportion to the total filled cell volume.

- The Cary 630 FTIR spectrometer scans quickly and thus in 60 seconds, approximately 148 scans are acquired at 4 cm^{-1} resolution. This is more than adequate to get an excellent transmission spectrum from virtually any liquid.

This application note demonstrates that a volatile solvent or solute has little or no evaporation from the open DialPath cell in the time period that is required to get an excellent spectrum, that is, under one minute. Two examples are shown to elucidate the effects of evaporation and diffusion on calibrated methods:

- Dioctyl phthalate (DOP, non-volatile analyte) in tetrahydrofuran (THF, volatile solvent).

- Benzene (highly volatile analyte) in hexane (volatile solvent).

Experimental and results

Measurement of DOP in THF

Analytical standards of dioctyl phthalate (DOP) in tetrahydrofuran (THF) were prepared volumetrically in the 0 to 5% range, and their FTIR spectra collected using the DialPath's 100 µm pathlength. The spectra of the standards were measured in triplicate collecting 64 scans at 8 cm^{-1} resolution, requiring an 18 second scan time. A quantitative calibration was developed using partial least squares (PLS) modeling of the DOP ester absorbance region; two loading vectors were used. The standard error of cross validation (SECV) for this method was 0.012% DOP; the actual versus predicted correlation coefficient was 0.9999.

Samples of DOP in THF at 0.5% nominal concentration were prepared volumetrically. The 0.5% sample was measured with the same method parameters (18 second scan time) with increasing delays from sample introduction to the start of scanning. Each sample was introduced with the cell in the closed position using a plastic transfer pipette (the solvent wicks into the cell very easily) and the cell was completely filled (~250 µL). Since the solvent is the volatile component, effects due to evaporation would increase the DOP concentration. Figure 2 shows the replicate measurements of samples t = 0, 30, 60, 120 second delay. The mean value for the 0 second delay is plotted as the red line and the 2% error limits are plotted as the two purple lines. Even at a 2 minute delay, little effect of the evaporation can be observed.

Measurement of benzene in hexane

In this analysis, a volatile solvent (hexane) and a highly volatile solute (benzene) were measured using the 100 µm pathlength. The volatility of these liquids represents a worst case scenario for evaporation effects on quantitative analysis, and tests the ability of the open cell design to handle volatile liquids.

A PLS model was created that used one loading vector, had an SECV of 0.0076% benzene and an actual versus predicted correlation coefficient of 0.9960. A benzene in hexane sample of 0.5% was prepared and used to test the repeatability at 0, 45 and 60 seconds delay between sample introduction and measurement. Figure 3 shows the results of each measurement as well as the average value of the 0 second delay samples as the red line and the 2% relative error levels as the red line. These results indicate that methods up to 60 seconds in length have minimal appreciable effect on measurement accuracy even for highly volatile samples.

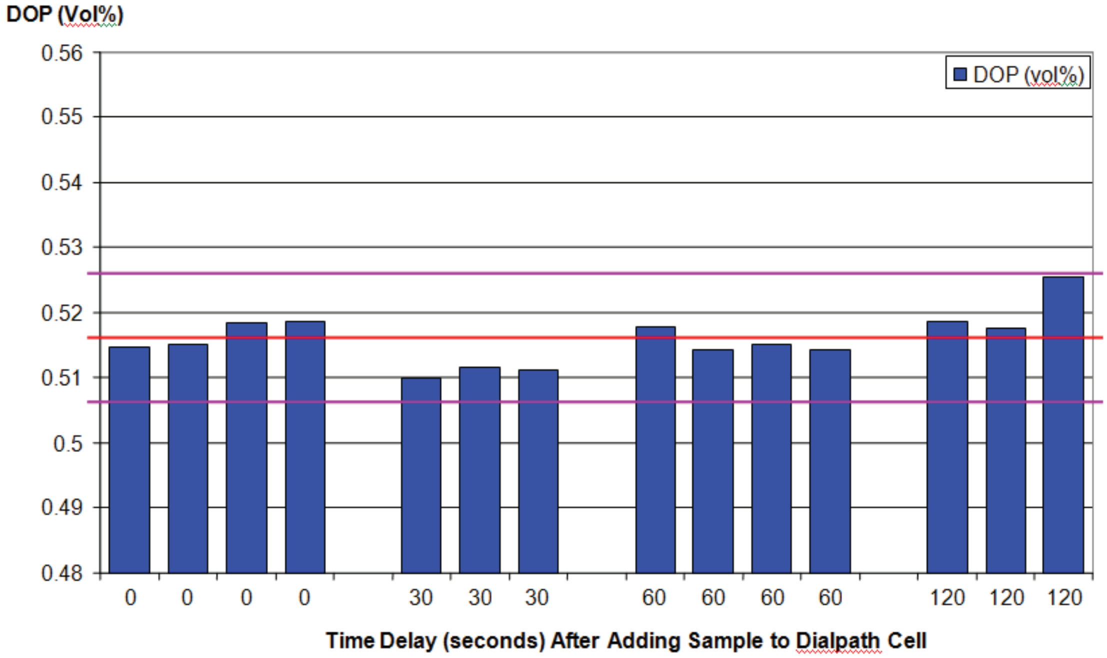

Figure 2. Testing the effects of solvent evaporation using the DialPath transmission cell. The dioctyl phthalate (DOP) vol% results from replicate measurements at increasing delays from sample introduction to DialPath cell and sample scan initialization. The red line is the mean measured DOP concentration with no time delay, and the ±2% relative error from mean time 0 is shown as purple lines.

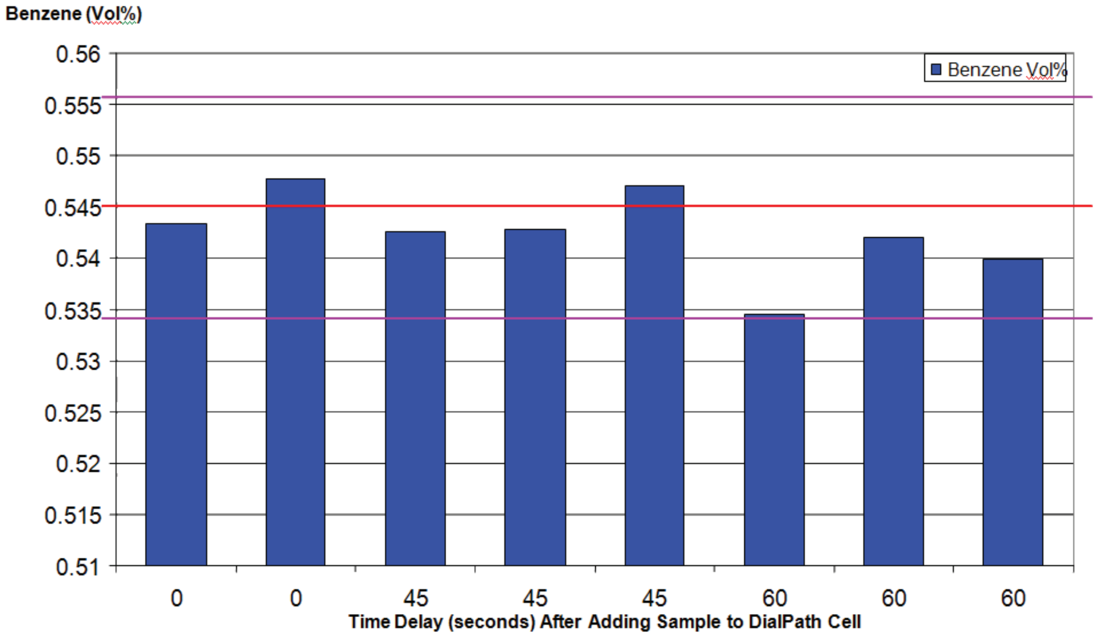

Figure 3. Testing the possible effects of solvent and solute evaporation using DialPath transmission cell. The benzene vol% results from replicate measurements at increasing delays from sample introduction to DialPath cell and sample scan initialization (18 s). The red line is the mean measured benzene % concentration with no time delay, and the ±2% relative error from mean time 0 is shown as purple lines.

Conclusion

The Agilent Cary 630 FTIR with DialPath technology effectively handles volatile liquids. Due to the fast scanning FTIR technology of the Cary 630, and the much slower rate of diffusion, there is essentially no observed effect due to evaporation in a normal (<60 second) measurement time. This is a result of the shape and configuration of the DialPath open cell design, since the active region requires just 3 µL of solvent in a total fill volume for the cell of 250 µL. This large difference between sampled and bulk cell volume coupled with the distance that the diffusion gradient has to travel before reaching the inner sampling region explains why no significant effects of solvent or solute diffusion or evaporation are observed using the DialPath accessory. The ease of use and simplicity of the DialPath technology makes it ideal for many volatile liquid applications including the analysis of gasoline, ethanol, reaction monitoring or solvent extraction.

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