Agilent Cary 630 with DialPath technology: effortless FTIR transmission spectroscopy of liquid samples

Application note

Chemical

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Introduction

Fixed pathlength, transmission IR spectroscopy provides fine spectral detail, which is important for quality-based measurements where subtleties or small variations differentiate “good” from “bad” materials. Since transmission cells can provide pathlengths that are significantly greater than that provided by ATR-based technology, they are more amenable to the measurement of lower concentration solutes. The downside to transmission cells, which have been used for over four decades, is that they are difficult to use when compared to ATR techniques.
Background and the use of fixed pathlength cells

For the past 40 years, the standard for liquid measurements is the fixed pathlength transmission cell. In this device, the optical pathlength is generated by the use of thin spacers sandwiched between a pair of infrared transmitting windows. Two versions of these cells are used; demountable cells and sealed cells. Demountable cells are dismantled to simplify “filling”, “emptying” and cleaning. The windows are separated, and the sample is dropped into the void in the spacer, and then the top window is carefully replaced to form a sandwich with the liquid; taking care not to trap air. The problem with this approach is that assembly can be difficult and there is uncertainty in the pathlength formed. At best, it is a semi-quantitative approach to sample handling.

Permanently sealed cells are required for accurate quantitative analysis of liquids. In a sealed cell, the sample holder, the windows and the spacers are permanently affixed. The cell is filled via special sample ports where the liquid is injected from a syringe. While this sounds simple, in practice it has significant practical drawbacks. Filling, where the liquid is “squeezed” into the confined space, which is at most 100 microns thick, is the first challenge. This can require the application of pressure from a syringe. This step requires extreme caution because the hydraulic pressure generated can damage the cell and can cause leaks. Teflon sheet spacers are used in demountable cells and occasionally in sealed cells. However, the sealing integrity of Teflon-based spacers is problematic.

Another important practical issue is emptying and cleaning the cell. They are usually filled and emptied by a pair of syringes connected to the filling ports of the cell. This action takes skill and dexterity, and if not carried out carefully it will lead to the formation of bubbles; a serious interference in the measurement. Incorrect use can lead to cell damage, with resultant leakage of fluid. Also, short pathlengths (less than 50 µm thick) are especially difficult to use with samples of medium to high viscosity. Emptying and cleaning are equally difficult, and again a syringe is used to draw out the sample, and then to flush solvent through the cell until the cell is clean.

DialPath – a better approach to Fixed Pathlength Infrared Measurements

Agilent’s DialPath technology features a rotary head equipped with three separate ZnSe windows. When a window on the rotating head is positioned above a second, fixed window located on the sampling platform, individual fixed pathlengths are created (Figure 1A). Figure 1B shows the head located at position 1, which provides a nominal 30 µm optical path; the other two locations provide nominal 50 µm and 250 µm paths, respectively.

![Figure 1. The DialPath sampling point concept (A): provides a user selectable pathlength, with one of three fixed/calibrated optical paths, designated 1, 2 and 3 (B).](image)

A drop of the liquid sample is placed on fixed window, the sampling head is rotated in place, and the measurement made. The liquid forms a uniform capillary film between the lower window and the window in the rotary head. The sweeping action of the rotary head produces a uniform film without any bubble interference. A slight curvature of the optical surfaces eliminates the formation of optical interference effects. With the DialPath technology it is as easy to fill, measure and clean liquid samples as with ATR, yet it provides the longer (and variable) pathlength required for many critical analyses.

It is appropriate to compare the spectral data from a standard diamond ATR system with the fixed pathlength (DialPath) measurement (Figure 2). Both systems provide good quality spectral data, however, characteristic details in the spectrum for property
measurements, such as the degree and type of unsaturation of an edible oil, requires the use of a long, fixed path measurement.

**Practical applications of a fixed pathlength measurement system**

A major benefit of the open architecture of the Cary 630 DialPath system is the ability to handle medium to high viscosity liquids. Typical applications that are constrained by viscosity are measurements on vegetable oils (including cooking and edible oils), dairy products (such as milk, cream and butter products) and automotive products, including fuels, lubricating oils and greases. While an ATR liquid measurement system might be used for some of these applications, the increased spectral detail of a longer pathlength is preferred for product quality and performance-related measurements. This is important for both edible and cooking oils and products derived from these materials, such as biodiesel fuels (Figures 3 and 4).

The role of mid-infrared in the commercial analysis of milk and dairy products is well established. The measurement of raw milk in a fixed pathlength cell is used by regulatory agencies to control and standardize milk and dairy products. Standard methods exist for fat and protein content, which is used for the payment of the primary producer. All of the relevant components in dairy products are derived from measurements of the infrared spectral data between 1800 cm\(^{-1}\) and 1000 cm\(^{-1}\), a region that includes fat (ester), protein (amide bands) and sugars/lactose (C-O-C, ether bands). Attempts to make these measurements in a standard sealed cell are fraught with difficulties. The accuracy of a fixed pathlength measurement is required, and the ease of handling high fat content materials, such as cream products, with the ease of cleaning, make the DialPath approach (Figure 5) ideal for dairy product analysis.
Summary - The DialPath advantage:

• Makes transmission spectroscopy of liquids as easy as ATR

• Instantly select one of three factory-calibrated, fixed pathlengths between 30 and 250 microns – ideal for both qualitative and quantitative analysis

• For lower concentration samples, simply dial-up a longer pathlength.

• For more concentrated samples, use a shorter pathlength.

• Simply place a drop of liquid between the two windows and analyze.

• No spacers, no leakage, no fringing, no expensive windows (or spacers) to replace.

• Autosamplers or syringes are not required for sample introduction.

• Effectively handle liquids of varying viscosity and volatility.

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