The DialPath Solution—an Easier Way to Analyze Liquids By FTIR

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Outline

- Background of FTIR Transmission Technology
- Traditional Transmission Cell
- ATR vs. Transmission
- DialPath/TumbIR introduction
- Agilent Mobile Spectrometers & MicrolabPC Software
- Applications
- Summary
IR Transmission

- Transmission techniques offer many advantages and should be used whenever possible, unless reliable sample preparation becomes too difficult, too time consuming or impractical.

- Transmission spectra are of the highest quality and are often used as references for the purpose of quantitative analysis. The basic measurements adhere to the Beer-Lambert law.

\[ A = a \cdot b \cdot c \]

- \( A = \) absorbance
- \( a = \) absorptivity
- \( b = \) pathlength
- \( c = \) component concentration

*The longer the pathlength, the stronger the Absorbance*
Transmission Cell

- Transmission Cells are used to make the IR transmission measurements.
- The choice of window material, pathlength, and window configuration are determined by the sample and the desired spectral ranges.
- If quantitative analysis is needed, a cell with known (or calibrated) pathlength must used.
- Due to the strong absorption of IR, IR cells are usually in the tens um - mm range.
- Due to the cost of the IR-transparent material, cleaning the cell windows is necessary.
- Traditional Transmission Cells......
Demountable Transmission Cell

A general purpose liquid transmission cell which can be easily disassembled. It comprises IR-transparent windows and appropriate spacers. Spacers of various thicknesses can be used to reach the desired pathlength. The sample is introduced via filling tubing/ports.

Applications

- Both qualitative and quantitative
- All liquids

Challenges

- Spectral reproducibility (Spacer-related)
- Tubing/port for sample addition
- “Easy” clean but still Time consuming especially when more samples need to be tested
Sealed Transmission Cell

In the sealed cell, the window pair and spacer are amalgamated as an assembly to ensure a constant pathlength for quantitative analysis. Samples added through tubing and port then flush-washed for cleaning.

Applications

- Volatile Liquids
- Quantitative Analysis
- Low Viscosity Liquids

Challenges

- Tubing/port for sample addition
- Need different pathlength
- Extreme difficult to clean (need repetitive flushing wash). Time consuming
- Fragile (e.g. Sealing rubber liable for erosion)
Mull Transmission Cell

The Mull Cell does **NOT** use the standard liquid filling ports. The sample is placed directly onto one of the circular windows and the other window is then placed on top. Designed for tough liquid samples.

**Applications**

- High Viscosity Liquids
- Gels, Pastes, oil and grease
- Suspension

**Challenges**

- Spacer contamination
- Poor reproducibility
- Window cost
ATR – Theory and Applications

- Attenuated Total Reflectance (ATR) is today’s most widely used FTIR sampling tool. The main feature of ATR sampling is the small depth of penetration (i.e. pathlength) of the IR beam into the sample (i.e. usually less than 1um), making it a virtually “surface” analysis.

- ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds sample analysis. The “open” sample interface allows easy sample cleaning. For liquid samples, simple rinsing and wiping would recover the crystal surface for new measurements.

- However, the advantage of small penetration depth could be a problem if larger pathlength is critical (e.g. high sensitivity quantitation). One solution is to improve the reflecting (bouncing) numbers.

While………..
Transmission vs. ATR

- Both Transmission and ATR can be used to study liquid samples, but they have clear differences.

- Transmission is a bulk testing and ATR is a surface testing (small penetration depth). Same results are expected only for homogeneous samples (e.g. a pure solvent or a stable solution).

- Different quantitation capability: Transmission has much better LOD (limit of detection) and LOQ (limit of quantitation) due to the larger pathlength.

- Transmission pathlength adjustment is relatively easier (distance-change). In comparison, to achieve higher ATR pathlength, more bouncing would be needed (size-change).
Transmission vs. ATR

To improve absorbance, simply increase $b$, (thicker sample). Same accessory.

To improve absorbance, have to increase bouncing numbers, (larger crystal). Different accessories.
Single Bounce vs. Multiple Bouncing ATR

Single Bounce ATR need very little or even no sample preparation. Almost all kinds of samples, solid/liquid/powder/gel/film can be effectively tested.

Multiple Bounce ATR provided greater absorption than single-bounce ATR and a easier sample handling than Dialpath. A very useful technology to test liquid samples.
DialPath: A Revolutionary Transmission Method

- **Precise and Customized Pathlength**
  - The distance between two transmission windows were precisely controlled, ensured great reproducibility.
  - DialPath offered three pathlength (Default 30, 50 and 100um).
  - TumbIR offered one of these three pathlength.
  - These pathlength can be customized to the proper value.

- **Easy Sample Handling**
  - Surface tension hold the sample perfectly between the transmission windows, the total volume need for testing are tens ul.
  - Liquid can be quickly wiped and cleaned for next testing.
  - As simple and easy as ATR.
Liquid Analysis Using the “DialPath”

Three steps to analysis

1. Ensure the crystal is clean
2. Place your sample on the window
3. Turn the DialPath to your required pathlength to analyze

4. Cleaning

https://www.youtube.com/watch?v=9BFqllGOfOY
Advantages of DialPath

- It permits nearly 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 port/tubs needed to introduce sample.
- 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.
- Little sample usage.
Mobile FTIR (Thanks to Smaller Interferometer)

1998 – Mini
Size: 10 ¼” x 12” x 4 ½”
Weight: 10 lbs.

2002 – Midget
Size: 4 ¼” x 2 ½” x 5 ¾”
Weight: 3.6 lbs

2007 – Micro
Size: 2 ½” x 2 ¾” x 4 ¼”
Weight: 1.9 lbs

2013 Nano
Agilent Mobile FTIRs with Dialpath/TumblIR

- Cary 5500: Yes
- Cary 630: Yes
- Cary 4500: Yes
- TopScan 4300: No
Dialpath allows customer to switch between three different path length (30-2000um)
Toluene has rich selection of spectral features, making it a perfect reference compound for pathlength calibration. The peak with different intensities can be used for different pathlength calibration.
Microlab PC – Method Driven Software

- Visually instruct users through collection
- User Levels
  administrator, certification, operator
- Methods
  data collection
  library search
  quantitative
- Results
  green, yellow, red display based on limits
- PC and Mobile
  full collection/prediction on mobile
  sync. between mobile and PC
Microlab PC – Quant Module

• The latest Microlab PC has embedded a Quant module, a Simple, guided methods development package for quantitative applications.

• Different Quant Algorithms allows single/multiple-component quantitations
  – Simple Beer’s Law
  – Classical Least Squares
  – Inverse Least Squares (Also known as Inverse Beer’s Law, or Multiple Linear Regression)
Microlab PC – Easy Report Generation

• MicrolabPC component formatting

• Microsoft Word Add-on enables easy report formatting

• Multiple template function

• PDF generation
Application 1: Volatile Liquid

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.

The expanded sample interface region of one of the cells (right). The relatively small ‘active region’ (3 µL fill volume – 50um pathlength) in proportion to the total filled cell volume minimizes the effects of evaporation and diffusion in the < 60 s time scale.

Agilent 5990-8540_EN_AppNote
Volatile Liquid

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

Testing DOP vol% results from replicates at increasing delays. The red line is the mean measured DOP concentration with no time delay, and the \( \pm 2\% \) relative error from mean time is shown as purple lines.

Agilent 5990-8540_EN_AppNote
Testing benzene vol% results from replicates at increasing delays. The red line is the **mean** measured Benzene concentration with no time delay, and the ±2% **relative error** from mean time is shown as purple lines.
Application 2: Waste Oil in Water

New advances in FTIR spectrometers allow them to be both sensitive and portable, making onsite analysis of oil in water possible.

Figure 1. The overlaid FTIR spectra of crude oil (blue) and mineral oil (red). The zoomed region indicates the local baseline (dashed line) used for the 1378 cm⁻¹ peak area measurement by FTIR.

Figure 2. The FTIR spectrum of cyclohexane measured on the Agilent 4500 FTIR spectrometer with a DialPath accessory. The inset zoom box illustrates the overlaid spectral region of measurement of the hydrocarbons (showing calibration standards 0–33 mg/L) using the methyl absorbance at 1378 cm⁻¹.
4500 Dialpath yield a LOD of 0.25 mg/L (0.25 ppm) and a LOQ of 0.75 mg/L (0.75 ppm) oil in water with an upper limit at 1000 mg/L (1000 ppm)

Figure 3. The mineral oil in cyclohexane calibration plot of actual (X-axis) versus predicted (Y-axis) values. The values displayed are the final concentrations of oil in water based on the ASTM D7678 parameters (900 mL water, 20 mL cyclohexane).
Application 3: Isotope in Body Fluid

Compared to isotope ratio mass spectrometry (IRMS), FTIR is also a valid measuring of deuterium oxide ($\text{D}_2\text{O}$) in human body fluids (mainly $\text{H}_2\text{O}$), but much faster, easier and cheaper.

![Plot of $\text{D}_2\text{O}$ concentration as measured by IRMS and an Agilent 4500 Series FTIR shows excellent correlation.](Agilent 5991-3531_EN_AppNote)
Isotope in Body Fluid

To date, the following limit of detection (3 × SD) values have been established for the measurement of $^2$H$_2$O in body fluids by the 4500 Series FTIR equipped with DialPath:

- Water 12 mg/kg
- Saliva 20 mg/kg
- Serum 18 mg/kg
- Urine 50 mg/kg

The speed and feasibility of FTIR make it possible to study the dynamic of D$_2$O loss in saliva.

*Agilent 5991-3531_EN_AppNote*
Application 4: Antioxidant in Polyethylene

Even optimized for liquid samples, Dialpath is not only limited to liquids. Solid samples such as thin films can be tested by Dialpath as well.

\[
\text{Wt\% Irganox 1010} = M \times \left( \frac{A_{1745}}{A_{2019}} \right) + N
\]

Where:
- Wt\% Irganox = Weight % of Irganox 1010 in the polyethylene
- \(A_{1745}\) = Absorbance of Irganox 1010 at 1745 cm\(^{-1}\)
- \(A_{2019}\) = Absorbance of polyethylene reference band at 2019 cm\(^{-1}\)
- \(M\) = Calibration constant
- \(N\) = Intercept
By calculating the peak ratio (defined in Microlab PC), the antioxidant component concentration can be quantified (LOQ ~0.01%--0.02%). The deviation was more from the thickness variation than from the spectrometer performance.

Agilent 5991-0457_EN_AppNote
Summary

- Agilent’s Dialpath technology is an easier way to Analyze Liquids by FTIR spectroscopy.

- Dialpath is bonded with Agilent mobile/portable FTIR systems and supported by the user-friendly MicrolabPC software.

- Dialpath provides advantages over traditional transmission cells by its easy sample deploying, window cleaning and more precise thickness control. It also provides multiple pathlength in the same accessory.

- Dialpath shows similar operational simplicity as ATR but its significantly larger pathlength makes it a more sensitive approach for liquid quantitation.