FTIR Spectroscopic Analyze on Aqueous Samples

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Background

- Fourier transform infrared (FTIR) spectroscopy is a versatile tool used to characterize various type of samples by differentiating origins, quantifying additives, detecting contaminants, monitoring degradation byproducts, fighting adulteration and so on.

- FTIR spectroscopy has become a widely used technique for quick, economic and multiplex assessing characteristics, and yet many people don't fully understand how it works and how to make it more efficient.

- Water, either as the target or the interferent, requires special attention in the sample treatment, technique selection and data manipulation. Due to complexity of the specimen and the testing goals, it is critical to understand water spectral features so that proper approaches can be carried to achieve accurate analysis..

Aqueous Specimen

- Aqueous samples refers to any specimen contain water components. Water can play the roles of solvents, ingredients or contaminants.
- The specimen can be of different states including liquid, solid, gas or others.
- Water (or moisture), a strong IR absorber, can be the target of analysis or the source of interference (depending on the application).

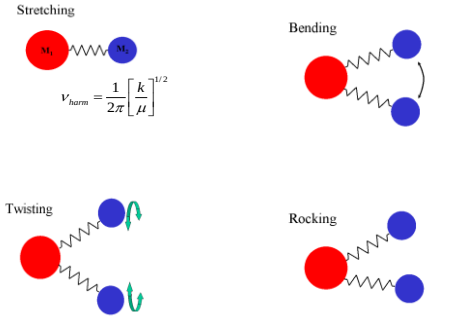
Principles of IR Spectroscopy

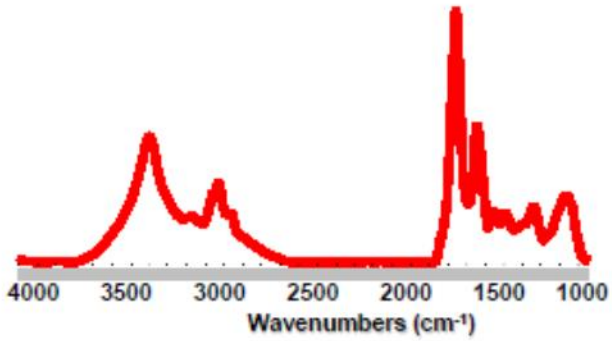
- Most organic molecules absorb light in the infrared region of the electromagnetic spectrum

- Absorption at certain frequencies or wavenumbers corresponds specifically to the bonds present

- Absorbance of the infrared light versus the frequency is the spectrum

- IR spectroscopy is for both qualification and quantification analysis





Why use FTIR in Chemical Analysis

➢FTIR spectroscopy is one of the most widely used laboratory tools for chemical analysis

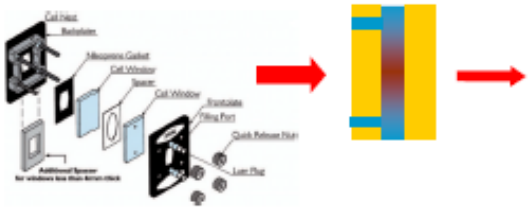
- Multiplex: — capable of detecting and quantifying multiple components and parameters simultaneously • e.g. moisture, alcohol, carbohydrate, protein...
- Easy to use: — No cumbersome sample preparation
- Inexpensive: — No reagents or wet chemistry required to reduce per measurement cost
- Fast: — replaces tedious and time-consuming physical and chemical methods
- High-throughput: —specified automation analyzer are available to handle massive amount of samples

Types of FTIR Sampling Techniques

Type of Analysis MODE:

Transmission/Absorbance

(liquids, gases, powders, films)

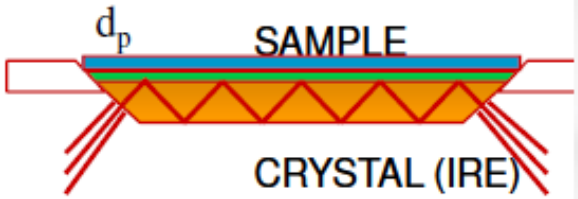


* Reflectance

(liquids, thins films,bulk materials)

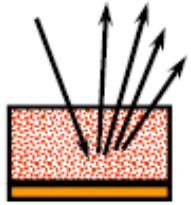
*ATR

(all, except gases)



*Diffuse Reflectance

(or DRIFT-mainly powders)

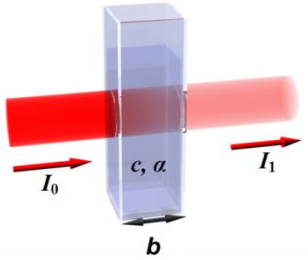


IR Transmission

- 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

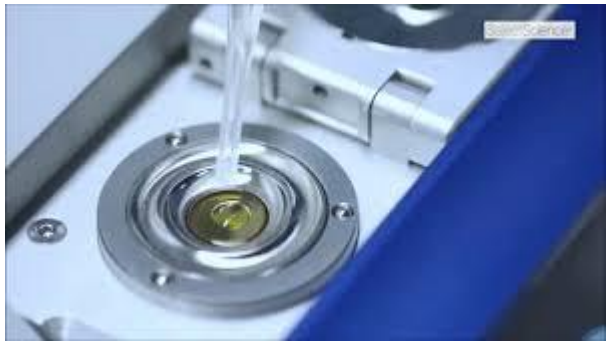
- Transmission Cells are used to make the IR transmission measurements.
- The choice of window material, pathlength, and window configuration are determined by the sample and the desired spectral ranges.
- If quantitative analysis is needed, a cell with known (or calibrated) pathlength must be used.
- Due to the strong absorption of IR, IR cells are usually in the 10um - 1mm range.
- Due to the cost of the IR-transparent material, cleaning the cell windows is necessary.
- Traditional Transmission Cells……

IR Transmission Devices

10cm Gas cell

Long-Path Gas cell

Demountable Liquid Cell



Pearl®

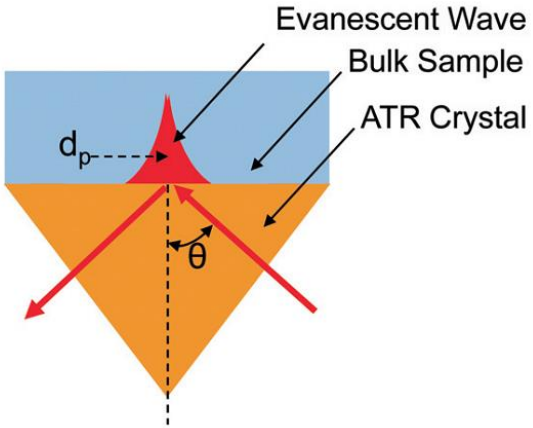
Dialpath®

➢Gas cell and liquid cell with different pathlength and operating process for transmission measurements.

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.

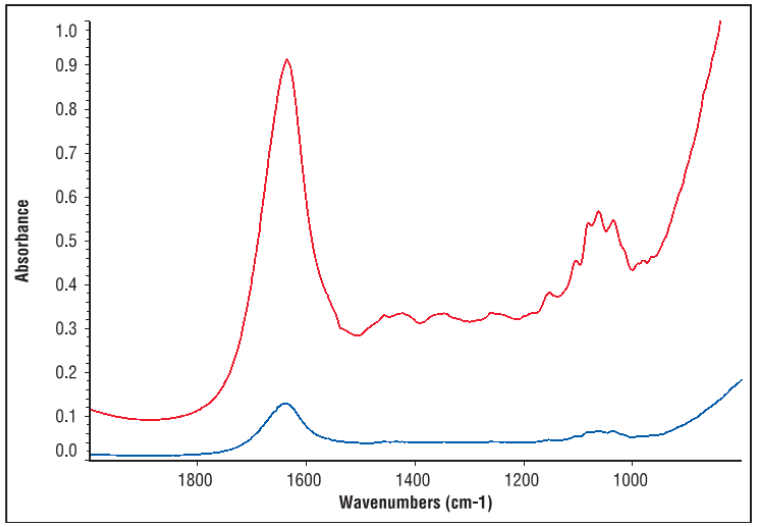
➢ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds sample analysis. The "open" sample interface allows easy sample cleaning . For liquid samples, simple rinsing and wiping would recover the crystal surface for new measurements.



➢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 increase the reflecting (bouncing) numbers.

➢While……

ATR – Penetration Depth



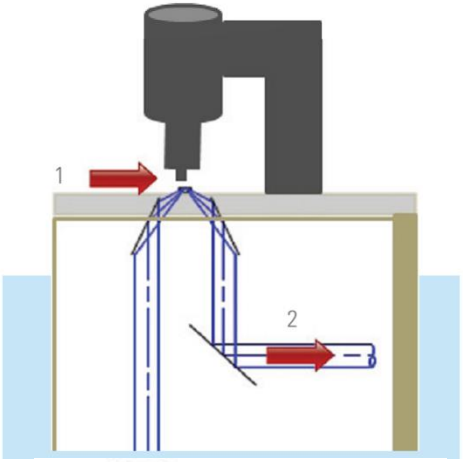
Soft Drink Sample using 10 Reflection and 1 Reflection ATR

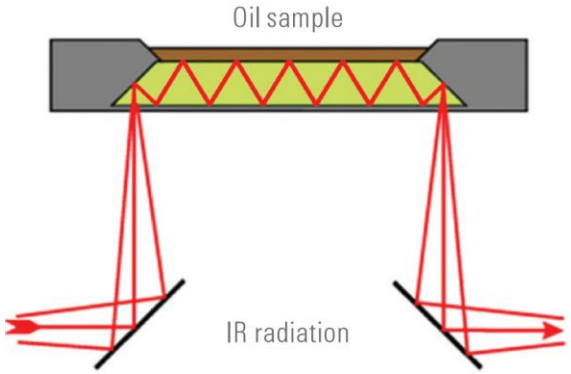
- Diamond-ATR vs. Ge-ATR
  - Refractive Index
  - Hardness
  - Cost
  - Different applications

	n_1	d_p, for $n_2 = 1.5$ $\lambda = 1000\ cm^{-1}$, 45 deg, microns
AMTIR	2.5	1.70
Diamond/ZnSe	2.4	2.01
Germanium	4.0	0.66

Single Bouncing 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.

Single Bounce

(Diamond/Ge/ZnSe)

Multiple Bounce

(ZnSe)

Transmission vs. ATR

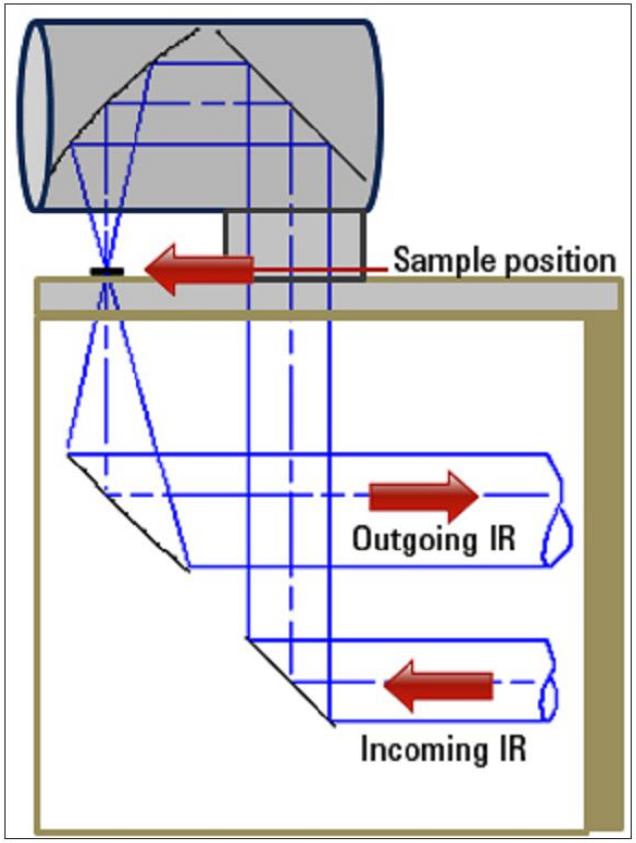
- Both Transmission and ATR can be used to study liquid samples, but they have clear differences.

- 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

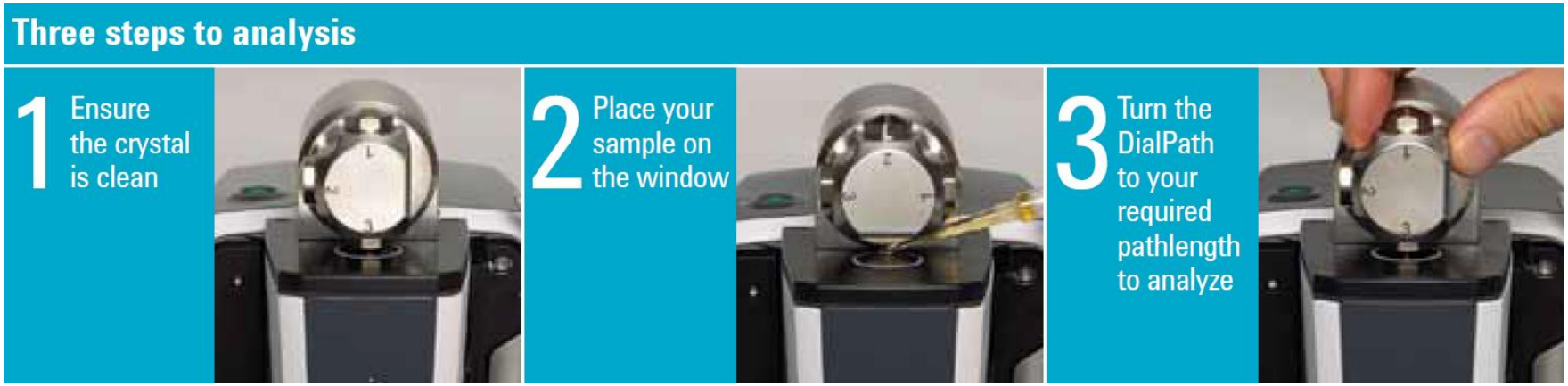
- Transmission pathlength adjustment is relatively easier (distance-change). In comparison, to achieve higher ATR pathlength, more bouncing number would be needed (size-change)

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)
  - TumblIR 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”



4. Cleaning

https://www.youtube.com/watch?v=rXsvk50Exsg

Specular Reflectance

➢Specular reflectance sampling in FTIR is a very important technique for measurement of thin layer substance on reflective substrates and analysis of bulk materials and measurement of monomolecular layers on a substrate material. The greatest advantage is that it provides a means of sample analysis with **NO** sample destruction---which is especially critical for fragile samples.

Types of specular reflectance experiments

- Reflection-Absorption of relatively thin films on reflective substrates measured at near normal angle of incidence
- Specular Reflectance measurements of relatively thick substances measured at near normal angle of incidence
- Grazing Angle Reflection-Absorption of ultra-thin films or monolayers deposited on surfaces measured at high angle of incidence

Diffuse Reflectance

- Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials.

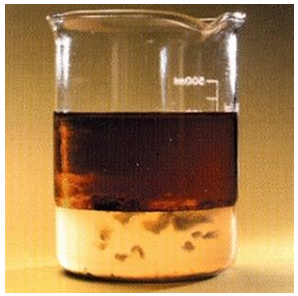
- Diffuse reflectance is an excellent sampling technique as it eliminates the time-consuming process of pressing pellets for transmission measurements.

- Diffuse reflectance can also be used to study the effects of temperature and catalysis by configuring the accessory with a heating or cooling environmental chamber.

- one of the greatest additional benefits of diffuse reflectance sampling is that it is ideally amenable to automation.

Water as the Target

- In some application, water component is the target of interests. For example:
  - Engine oil moisture quantitation
  - Chemical hygroscopicity
  - Dry fruit water content
  - Protective coating
  - Tablet moisture
  - ……



- ATR, diffuse reflectance and specular reflectance are used

- Due to the strong absorption of water molecules. Those tests are usually of high sensitivity and accuracy.

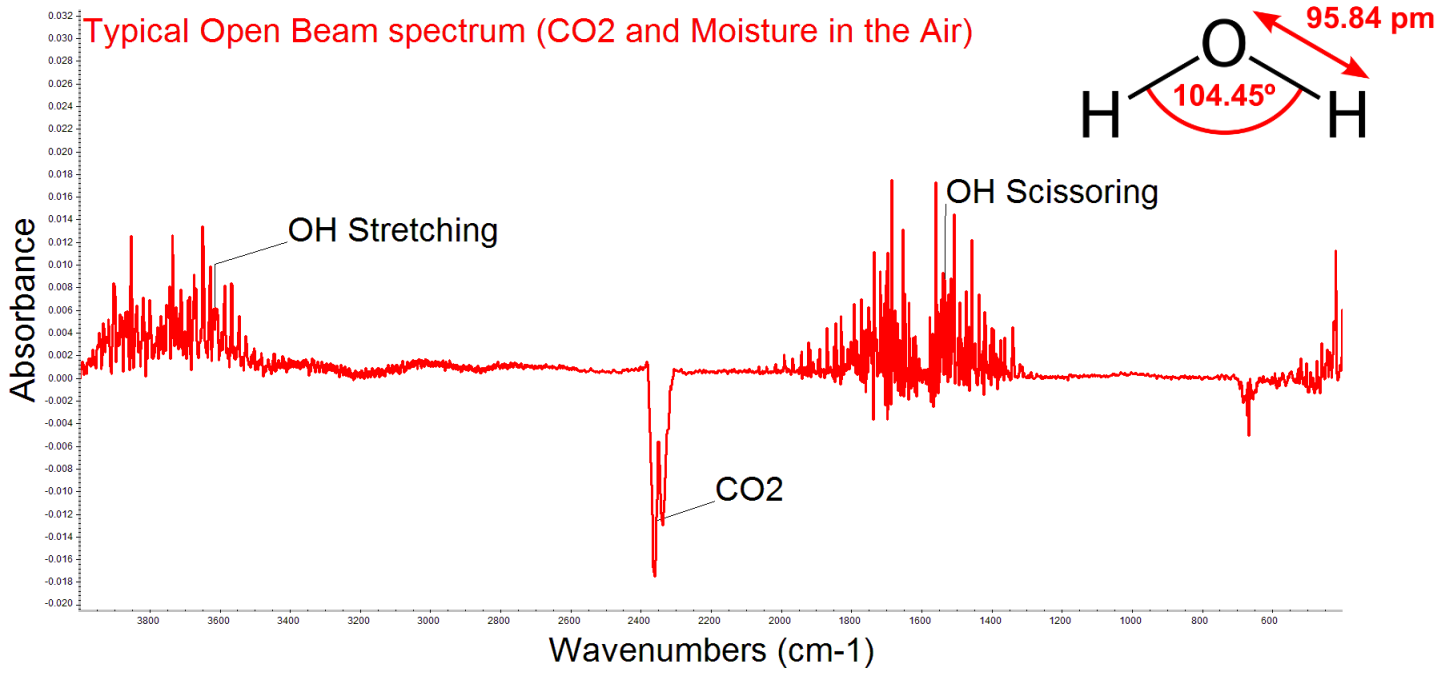
Water as the Interferent

- In most of the applications, water component is NOT the target of interests. It may be the matrix solvent of the specimen. The intense absorption now become a draw back because water spectral features may seriously interfere the analysis of the true target of interests.

- Different approaches are needed to overcome the interference so that most efficient testing can be done.

- Approach selections are determined by testing mode, window material selection, sample treatments, data handling and etc.

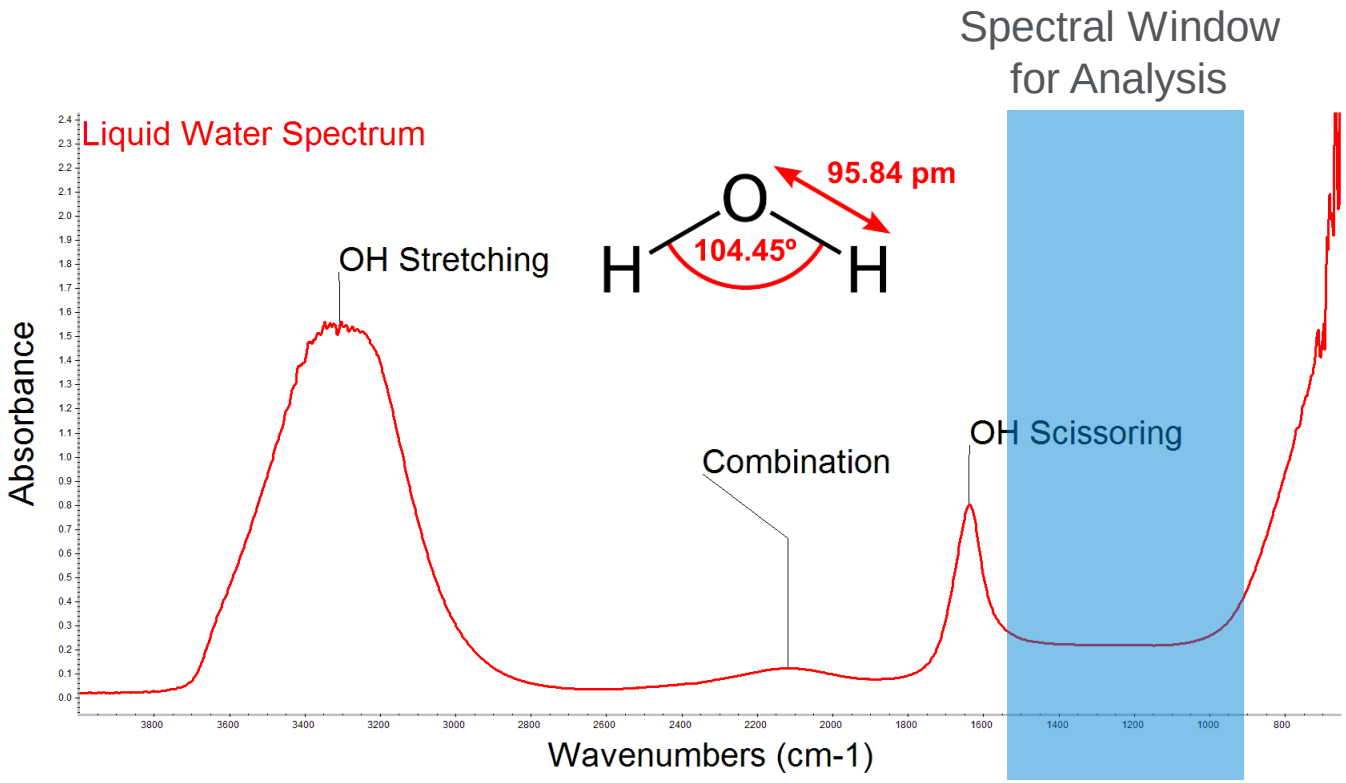
Water Vapor



- Gaseous-state Water and CO_2 are two major noise sources in IR spectroscopic measurements. Water vapor spectral features are usually spikes around 3900-3400 and 2000-1400.

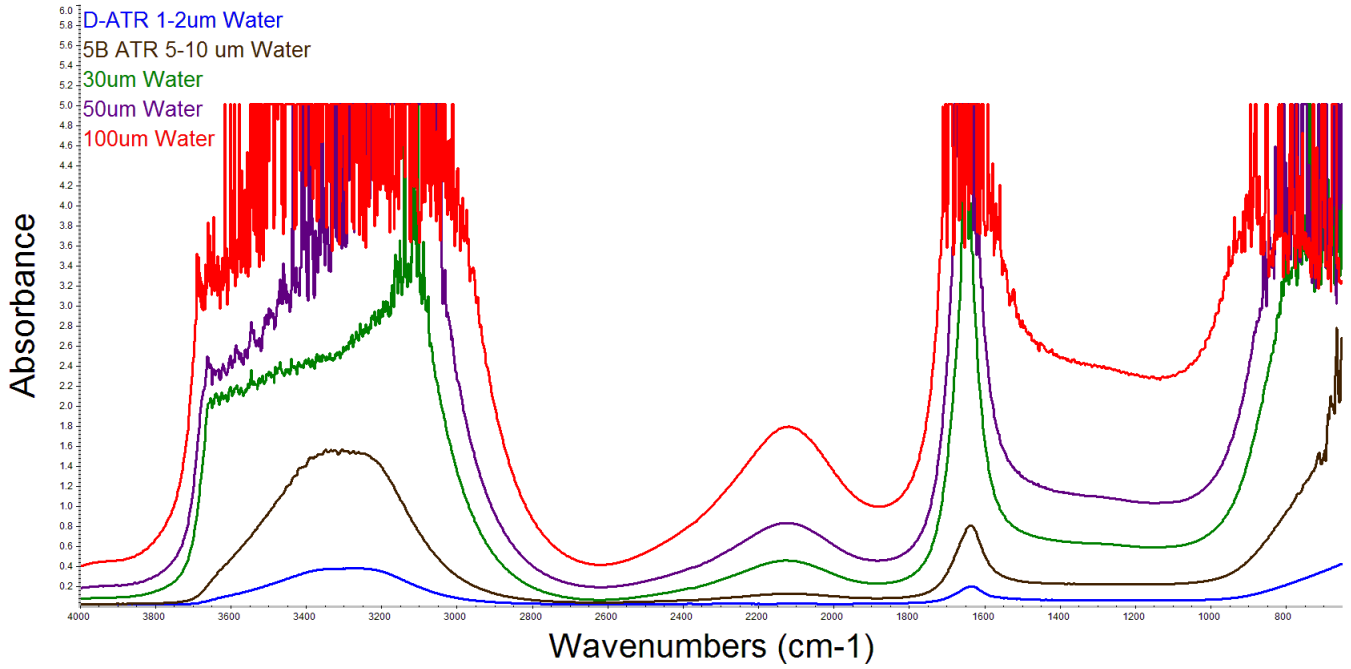
- Water from environment can be efficiently reduced or eliminated by sufficiently purging. If purging is not applicable, then the moisture should be kept stable to reduce fluctuation.

Water Liquid



- Liquidous water (and ice) show intense broad absorption bands between 3800-2900cm-1, 1700-1600cm-1 and below 900cm-1. those bands are liable to saturate and thus leaves limited spectral window for analysis (blue region).

Pathlength Influence on Liquid Water Spectra



- If the target features are 1500-1000, the preferred pathlength should be <50um.
- If the target features are 1700-1600, the preferred pathlength should be <10um.
- If the target features are 3800-2800, the preferred pathlength should be <5um

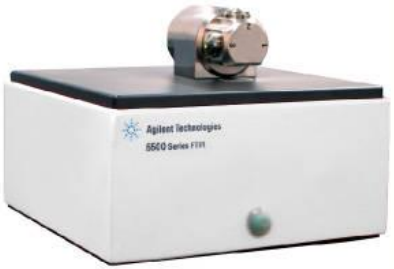
IR Substrate/Water Compatibility

Name	Properties / Typical Applications
Calcium Fluoride (CaF_2)	Low Absorption, High Refractive Index Homogeneity Used in Spectroscopy, Semiconductor Processing, Cooled Thermal Imaging
Fused Silica (FS)	Low CTE and Excellent Transmission in IR Used in Interferometry, Laser Instrumentation, Spectroscopy
Germanium (Ge)	High n_d, High Knoop Hardness, Excellent MWIR to FIR Transmission Used in Thermal Imaging, Rugged IR Imaging
Magnesium Fluoride (MgF_2)	High CTE, Low Index of Refraction, Good Transmission from Visible to MWIR Used in Windows, Lenses, and Polarizers that Do Not Require Anti-Reflection Coatings
N-BK7	Low-Cost Material, Works Well in Visible and NIR Applications Used in Machine Vision, Microscopy, Industrial Applications
Potassium Bromide (KBr)	Good Resistance to Mechanical Shock, Water Soluble, Broad Transmission Range Used in FTIR spectroscopy
Sapphire	Very Durable and Good Transmission in IR Used in IR Laser Systems, Spectroscopy, and Rugged Environmental Equipment
Silicon (Si)	Low Cost and Lightweight Used in Spectroscopy, MWIR Laser Systems, THz Imaging
Sodium Chloride (NaCl)	Water Soluble, Low Cost, Excellent Transmission from 250nm to 16µm, Sensitive to Thermal Shock Used in FTIR spectroscopy
Zinc Selenide (ZnSe)	Low Absorption, High Resistance to Thermal Shock CO_2 Laser Systems and Thermal Imaging
Zinc Sulfide (ZnS)	Excellent Transmission in Both Visible and IR, Harder and More Chemically Resistant than ZnSe Used in Thermal Imaging

Agilent FTIR Portfolio

Cary 630 Entry-level FTIR

Cary 610/620 FTIR Microscopes



5500 Series

4500 Series Portable FTIR

4200 FlexScan FTIR

4100 ExoScan

4300 TopScan

Choosing Proper FTIR Technology

- Sample Properties
  - States (Liquid, Solid, Powder, Gels, Grease or ….)
  - Safety (Poisonous, Contamination)
  - Homogeneity, Viscosity, Adhesion, Volatility, Moisture Level
  - ……
- Operation Consideration
  - Sample Treatments (Grinding, Extraction, Filtration …..)
  - Availability (Volume)
  - Cleaning
  - In-lab or in-Field
  - Numbers of samples (High-throughput, automation?)
- Analytical Expectation
  - Quantify or Qualify
  - Sensitivity (LOD, LOQ)
  - Reproducibility
  - Validation

ATR: An Universal Approach

- ATR is usually the 1st option as an “universal” technique for all type of samples except for gas.
- Minimum or no sample preparation are needed. Require firm physical contact (pressure for solids)
- Easy cleaning to recover the crystal
- A surface technique for both qualification and quantitation, but sensitivity is restricted due to penetration depth (i.e. 1-2um for single-bounce Diamond-ATR)
- Less interfered by moisture.
- Used both in-lab and in-field

Liquid Transmission: Bulk Study and Quantitation

- For liquid samples, if higher sensitivity and the bulk study is needed, transmission mode is the best choice.
- The higher sensitivity associated with the longer pathlength is especially crucial to quantitation. (e.g. ppm level LOD can be achieved only in transmission mode)
- Cleaning of the transmission cell is the bottleneck of the traditional transmission cells, Dialpath is as easy as ATR
- Automation transmission have been available to handle massive amount of sample (e.g. dairy analyzer, wine analyzer)

Solid Transmission: X-sectioning or Pellet-Making

- Solid transmission measurements usually involve sample preparation. IR-transparent samples must be made through X-sectioning (usually by microtome) or Pellet-making.
- Special equipment is usually needed for the sample preparation
- Due to the complexity of the procedure, solid transmission has been almost completely replaced by ATR in routine IR measurements.
- Solid transmission is still widely utilized in FTIR microscopy.

Diffuse Reflectance: Powder and Scattering Surface

- For high scattering samples such as powder and rough samples, diffuse reflectance could be a proper technique.
- DR is a true non-destructive technique because no pressure (or even no contact) is needed (e.g. fragile samples, living fruits).
- Easy operation for in-field applications such as soil study.
- DR is less sensitive than transmission and ATR, but more convenient.
- DR is a widely used in-field.

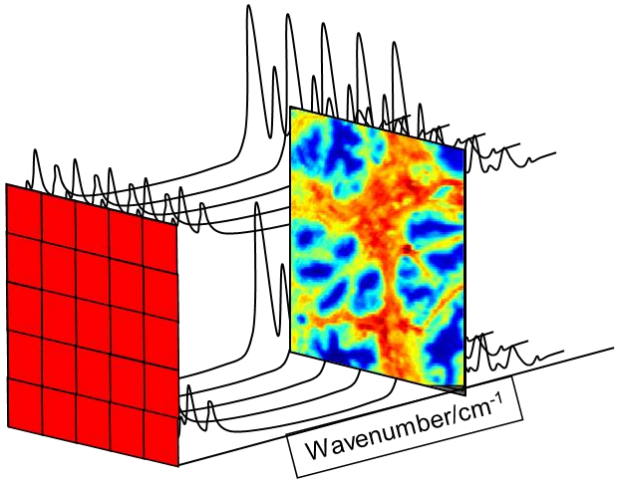
Lab Testing vs. Field testing

Lab Testing

Field Testing

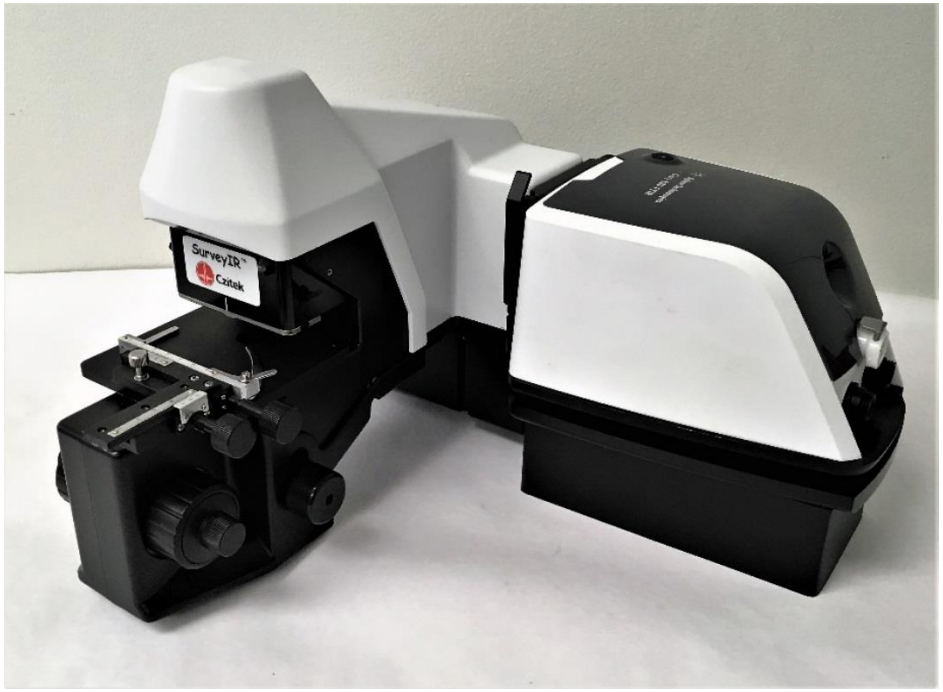
- Lab testing yield more comprehensive results (e.g. FTIR can be combined with elemental analysis), but requires longer turn-around time.
- Field testing yield fast response so that immediate actions can be taken before major problems. For example, grape sugar content can de determined in the field
- Agilent has solution for both.

FTIR Microscopy



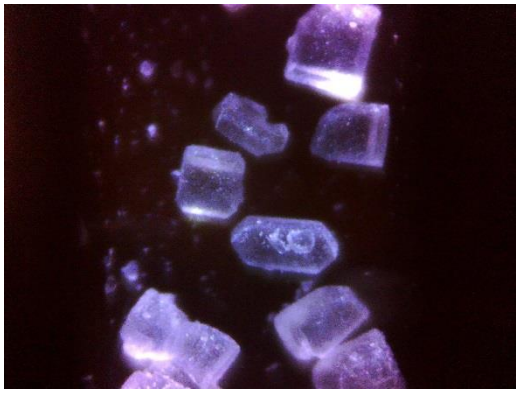
- An FTIR microscope allows users to visually see small (micron) sized samples and Collect accurate FTIR spectra from small samples so that both spatial and spectral information can be achieved.
- Running on single detector, linear array and 2-D focal plan array
- Running sample with transmission, reflectance, transflectance and ATR mode.
- Spatial resolution as good as 1.1um

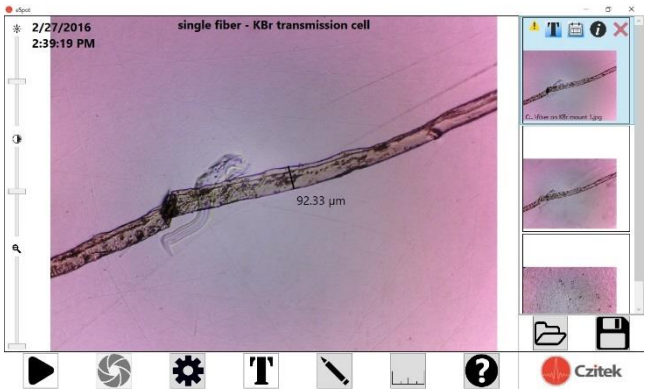
Cary 630 with SurveyIR Microscope



SurveyIR™ – The Microscopy Accessory for Cary 630 FTIR

- **Affordable performance**
  - Full FTIR microscope capabilities
  - Upgrade for any Cary 630
  - No maintenance requirements
- **Identify small samples**
  - black spots, fibers, paints, drugs, surface contaminants
- **See your samples – clearly, easily**
  - Integrated video with eSpot™ Software
  - Transmitted, reflected and oblique illumination
- **Measure any sample**
  - Reflection
  - ATR (diamond or germanium)
  - Transmission
- **Easy, valuable answers**
  - Customer installable
  - Minimal training





Application: Waste Oil in Water

To reduce water interference, an effective way is concentrate or even extract the target molecules. Once water is reduced or removed, longer pathlength can be used.

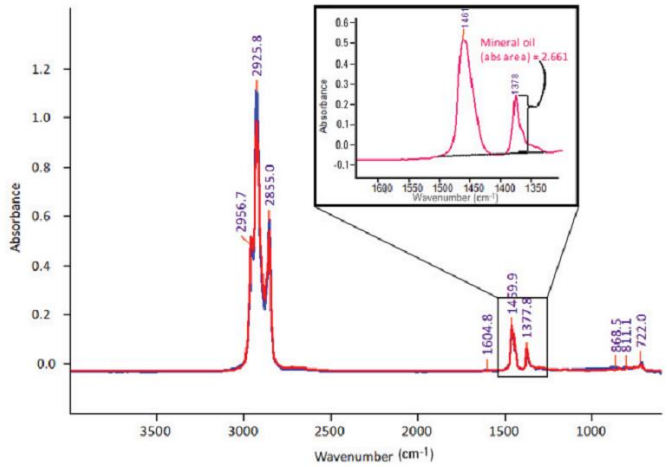


Figure 1. The overlaid FTIR spectra of crude oil (blue) and mineral oil (red). The zoomed region indicates the local baseline (dashed line) used for the 1378 cm^{-1} peak area measurement by FTIR.

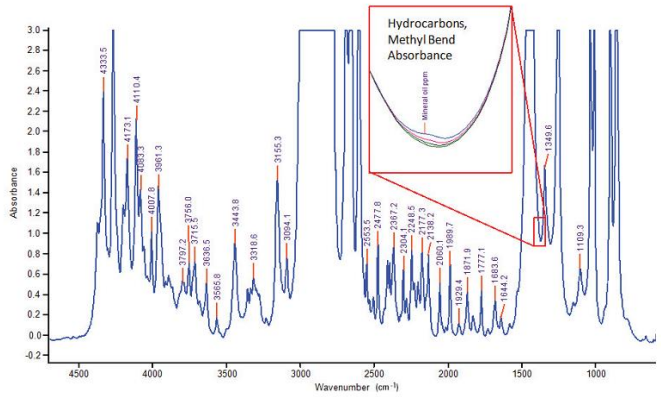
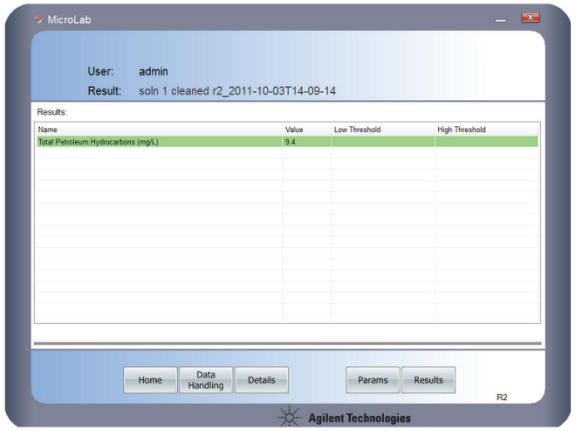


Figure 2. The FTIR spectrum of cyclohexane measured on the Agilent 4500 FTIR spectrometer with a DialPath accessory. The inset zoom box illustrates the overlaid spectral region of measurement of the hydrocarbons (showing calibration standards 0–33 mg/L) using the methyl absorbance at 1378 cm^{-1}.

Agilent 5990-9806EN_AppNote

Waste Oil in Water



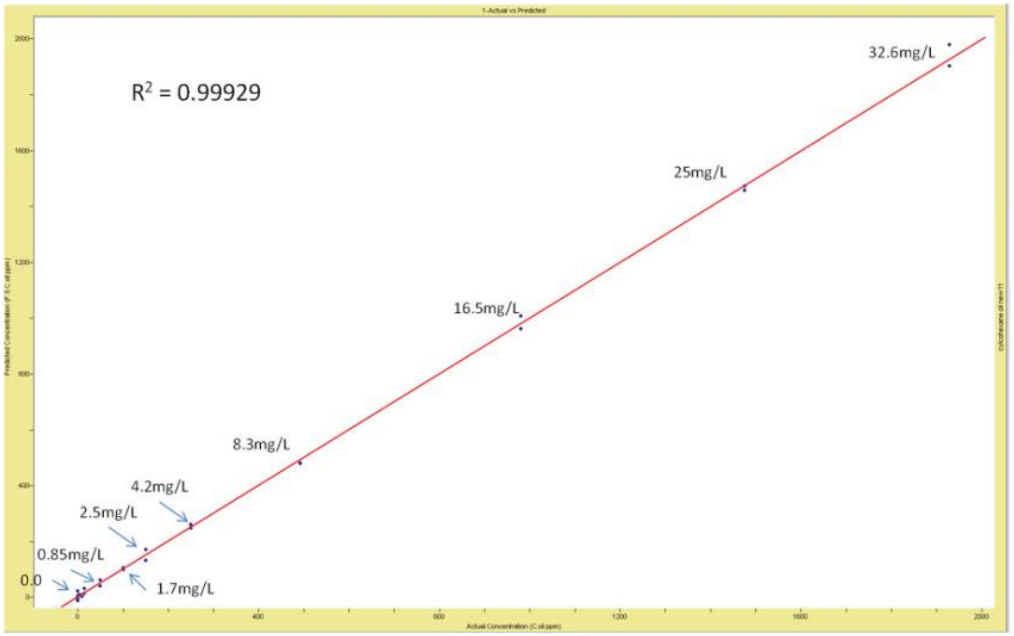


Figure 3. The mineral oil in cyclohexane calibration plot of actual (X-axis) versus predicted (Y-axis) values. The values displayed are the final concentrations of oil in water based on the ASTM D7678 parameters (900 mL water, 20 mL cyclohexane).

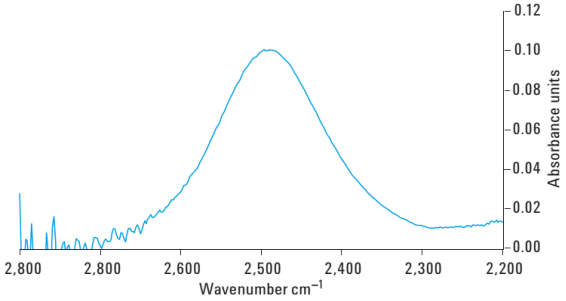
4500 Dialpath yield a LOD of 0.2 mg/L (0.25 ppm) and a LOQ of 0.75 mg/L (0.75 ppm) oil in water with an upper limit at 1000 mg/L (1000 ppm)

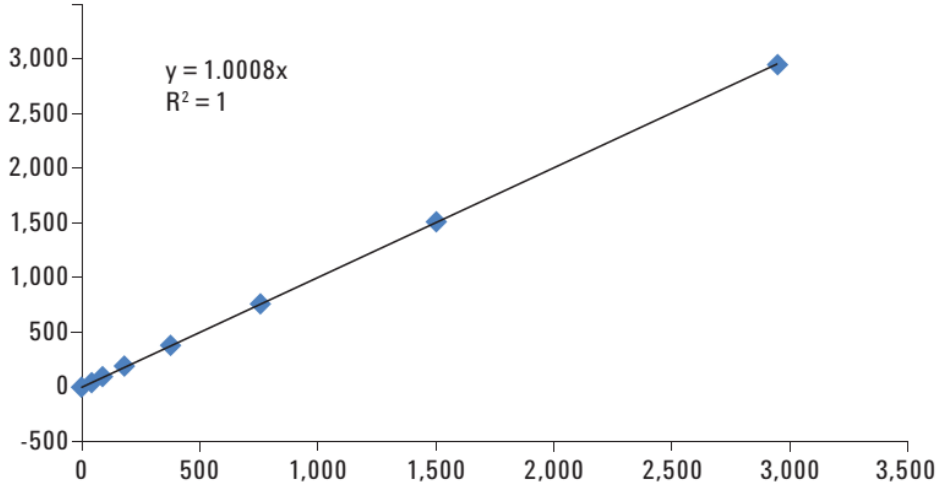
Agilent 5990-9806EN_AppNote

D_2O Quantitation

FTIR is a valid quantitative approach of **deuterium oxide (D_2O)** in fluids (mainly H_2O). By using the unique around 2500cm-1, long pathlength can be used so that low limit of detection (as low as 10ppm) is possible.

100um pathlength



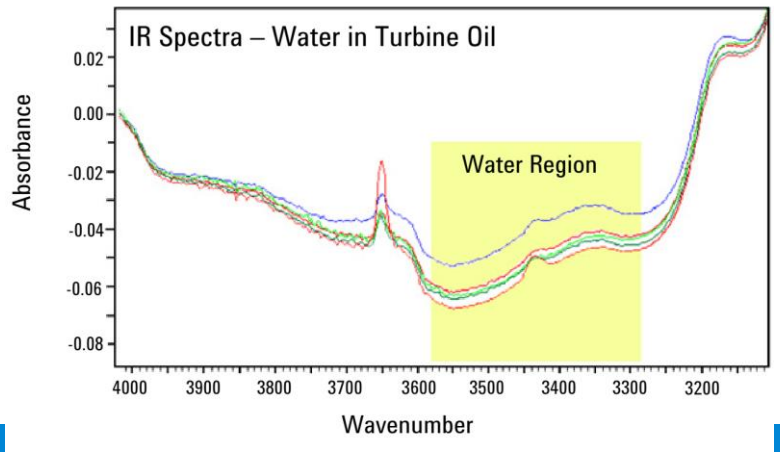


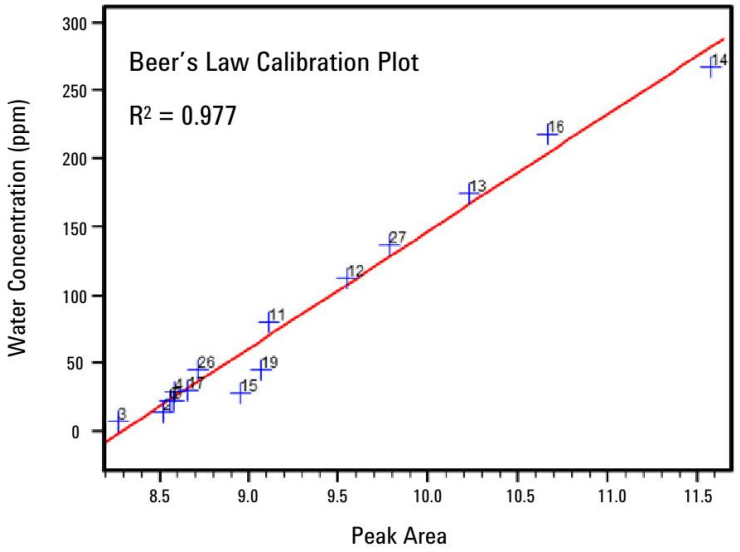
Plot of D_2O concentration as measured by IRMS and an Agilent 4500 Series FTIR shows excellent correlation.

Agilent 5991-3531_EN_AppNote

Onsite Water Analysis in Turbine Oil

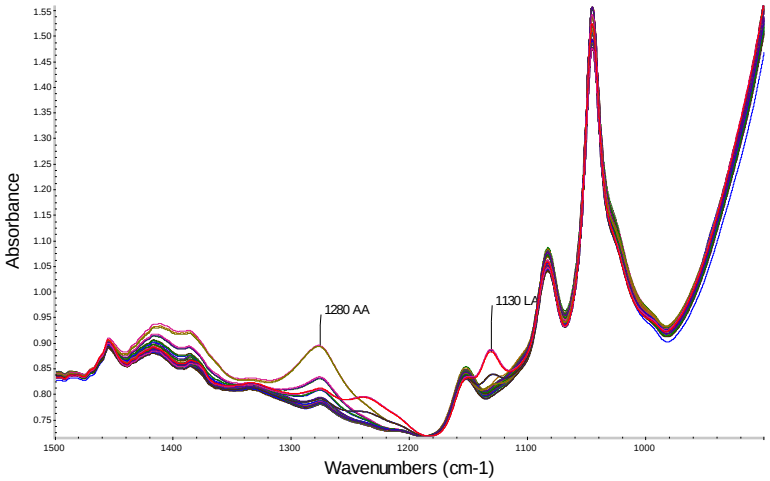
- The amount of water in turbine oil is critical to the performance and longevity of the equipment..
- The ability to measure water on-site, as soon as possible after drawing the sample, is a substantial benefit in obtaining accurate water level results. Agilent
- Cary 5500 with Dailapth liquid transmission accessory achieved ~30ppm LOD

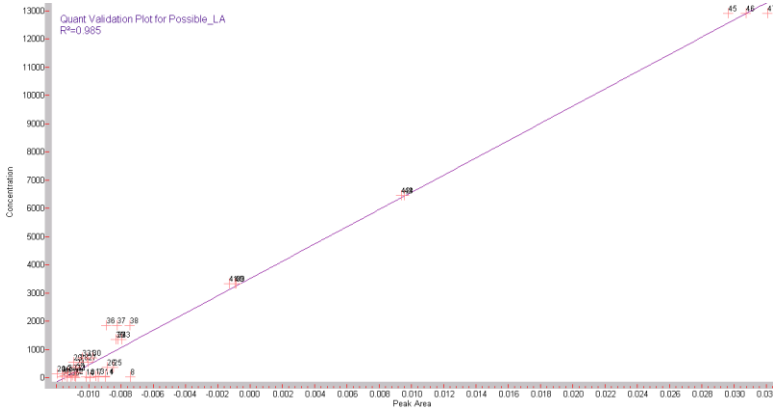




Beer Formulation Study with FTIR

- Beer with different ingredients may have significantly different flavor.
- The ability to quantify low level ingredients is critical to beer formulation
- Cary 630 with Dailapth liquid transmission accessory is used to quantify Lactic Acid (LA) and Acetic Acid (AA) in beer at the same time.

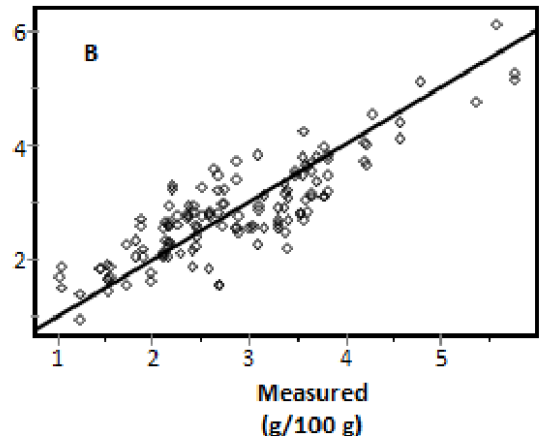




Tomato Screening with FTIR

- Soluble solid (i.e. Glucose, Citric acid and etc.) analysis is a important step for tomato quality control.
- Handheld FTIR with ATR accessory is proved to be a valid way for fast quality screening.

Tomato Analyte	Spectrometer	Concentration/pH Range	SECV	R
Brix	Benchtop	4.40 - 7.50	0.36	0.79
	mobile		0.39	0.75
Fructose	Benchtop	1.37 - 5.70 g/100g	0.32	0.87
	mobile		0.43	0.79
Glucose	Benchtop	1.03 - 5.75 g/100g	0.43	0.89
	mobile		0.49	0.86
pH	Benchtop	3.90 - 4.76	0.06	0.92
	mobile		0.06	0.91
Titratable Acids	Benchtop	0.27 - 0.88	0.05	0.91
	mobile		0.05	0.87
Citric Acid	Benchtop	256.37 - 2015.93 mg/100g	136.50	0.90
	mobile		123.40	0.92



Agilent 5991-3818_EN_AppNote

Summary

- There are massive variety type of aqueous samples, which require proper selection of FTIR testing techniques.

- Several critical judgements may help to evaluate the priorities of a technique

    - Sample Properties
    - Operation Consideration
    - Analytical Expectation

- Agilent FTIR products Wide selection of sampling interfaces can meet the challenges of different applications

QUESTIONS?