How to Choose Proper FTIR Spectroscopic Techniques to Analyze Petroleum Products

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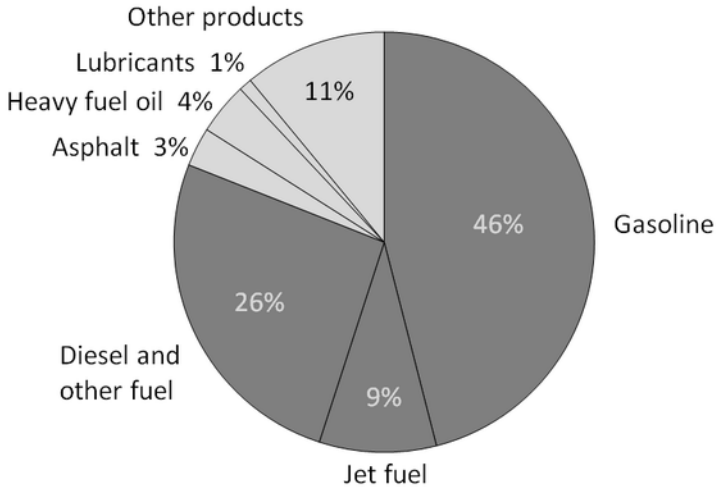
Petroleum Products



- Petroleum products are materials derived from crude oil (petroleum) as it is processed in oil refineries. Petroleum products are usually **complex** mixtures.
- The majority of petroleum is converted to petroleum products, which includes several classes of fuels, lubricants, waxes and asphalt.

Petroleum and Petroleum Products

Crude Oil

Grease

Asphalt

Gasoline

Heavy Fuel Oil

Lubricant

- Due to the various properties of petroleum products, proper FTIR techniques must be carefully selected to achieve best analytical outcome.

Petroleum and Petroleum Products

Product	Property	Analysis
Crude Oil	High viscous liquid, High absorption, non-volatile	Qualification and Quantification Analysis
Light Fuels (Gasoline, Kerosene, Diesel)	Low viscous liquid. Volatile	Adulteration, Contamination, Moisture.
Lubricants (Virgin)	Medium viscous liquid, non-volatile	Moisture, Oxidation, Aging, Degradation, Contamination…
Lubricants (Used)	High viscous liquid, High absorption, non-volatile	
Heavy Fuel oil	High viscous liquid, Difficult to clean	Component Analysis,
Grease	Deformable gel, Difficult to clean	Composition, Contamination…
Asphalt	Solid when cold, grease-like if heated. High absorption.	Degradation, mixing ratio….

Background

- Fourier transform infrared (FTIR) spectroscopy is a versatile tool used to characterize petroleum products by quantifying additives, detecting contaminants, monitoring degradation byproducts and fighting adulteration.
- FTIR spectroscopy has become a widely used technique for quickly assessing petroleum product characteristics, and yet many people don’t fully understand how it works and how to make it more efficient.
- Due to the different properties and testing goals, it is critical to choose the proper technique to facilitate the analyze of petroleum products.

Why use FTIR in Petroleum Product Analysis

- FTIR spectroscopy is one of the most widely used laboratory tools for petroleum product analysis

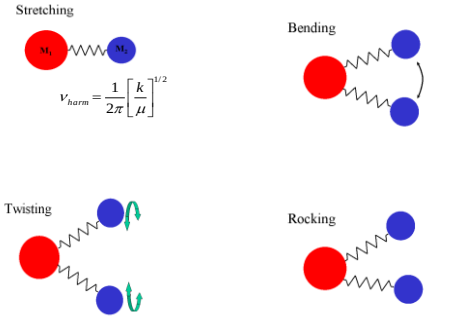
  - Multiplex: — capable of detecting and quantifying multiple components and parameters simultaneously • e.g. moisture, alcohol, glycol, soot, oxidation, nitration...
  - Easy to use: — No cumbersome sample preparation
  - Inexpensive: — No reagents or wet chemistry required to reduce per measurement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

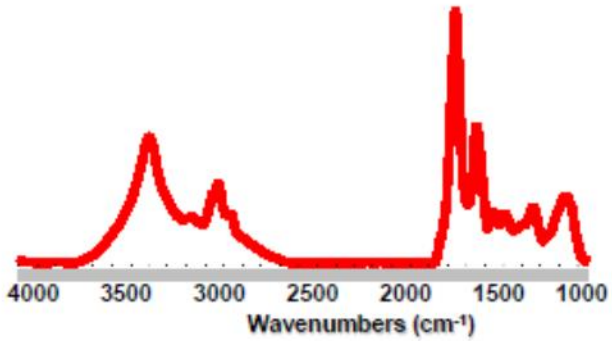
ASTM Methods of Petroleum Products with FTIR

- **ASTM D7371 – 14**: Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)
- **ASTM E2412 – 10**: Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using FTIR Spectrometry.
- **ASTM D7418 – 12**: Standard Practice for Set-Up and Operation of FTIR Spectrometers for In-Service Oil Condition Monitoring.
- **ASTM D7678 – 11**:Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy
- …….

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

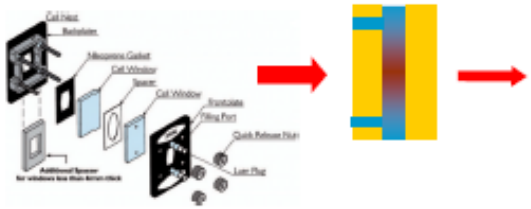




How is an IR Spectrum Collected?
Types of FTIR Sampling Techniques

Type of Analysis MODE:

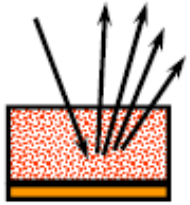
Transmission/Absorbance
(liquids, gases, powders, films)



*ATR
(all, except gases)

* Reflectance
(liquids, thins films,bulk materials)

*Diffuse Reflectance
(or DRIFT-mainly powders)

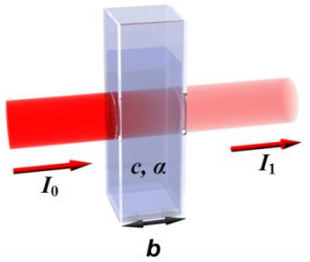


IR Transmission

- 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



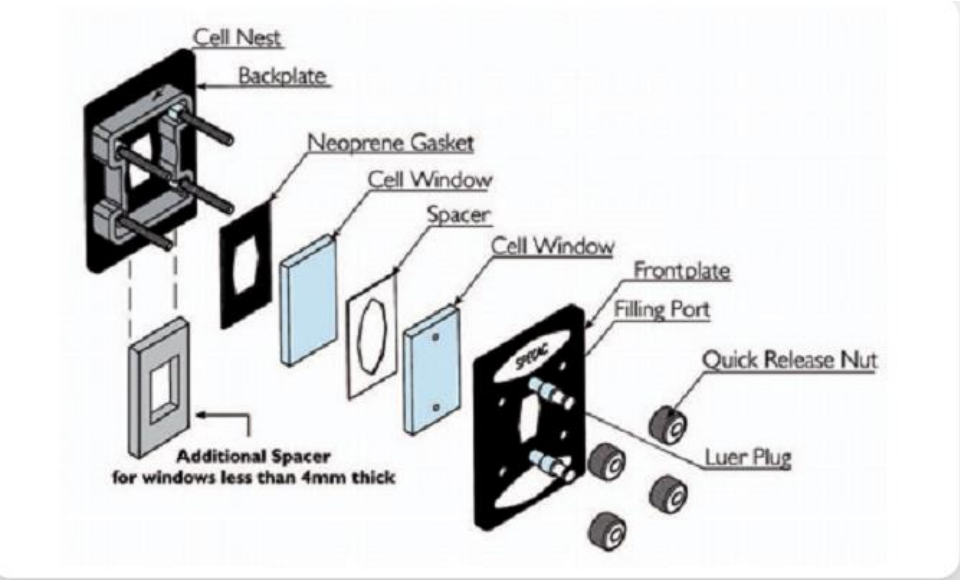
* The longer the pathlength, the stronger the Absorbance

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 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……

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

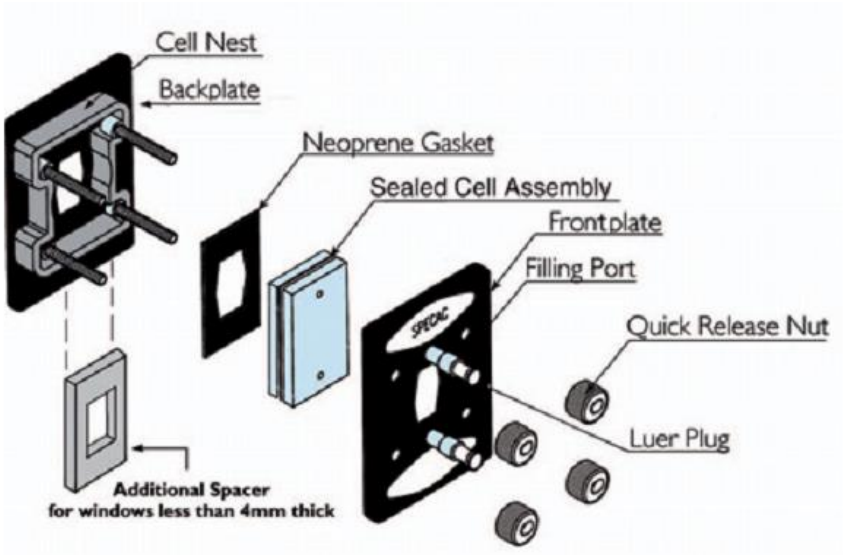
- Both qualitative and quantitative
- All liquids

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

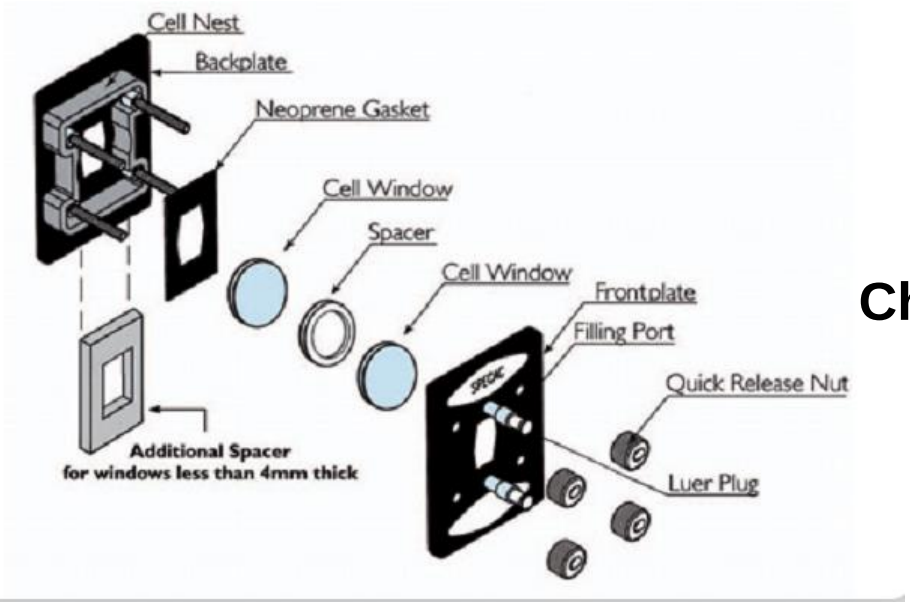
- Volatile Liquids
- Quantitative Analysis
- Low Viscosity Liquids

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

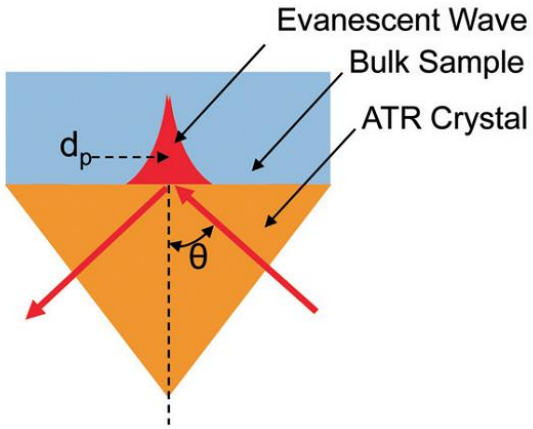
Challenges

- Spacer contamination
- Poor reproducibility
- Window cleaning

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.

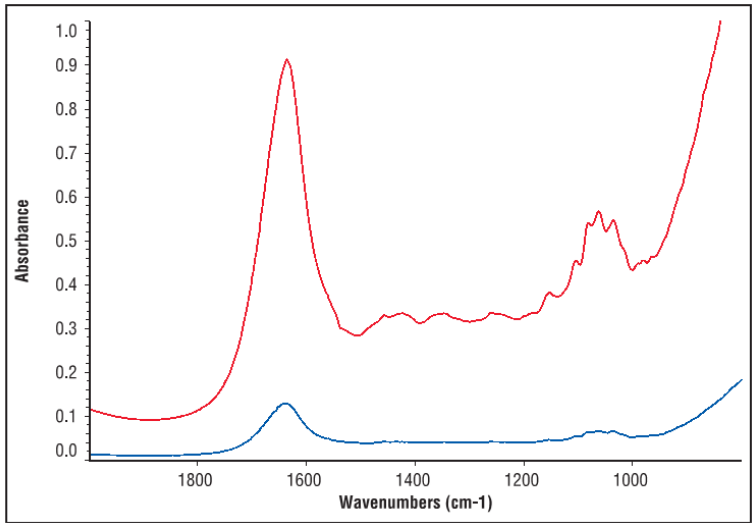
- ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds sample analysis. The "open" sample interface allows easy sample cleaning . For liquid samples, simple rinsing and wiping would recover the crystal surface for new measurements.



- 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……

ATR – Refractive Index vs. Penetration Depth

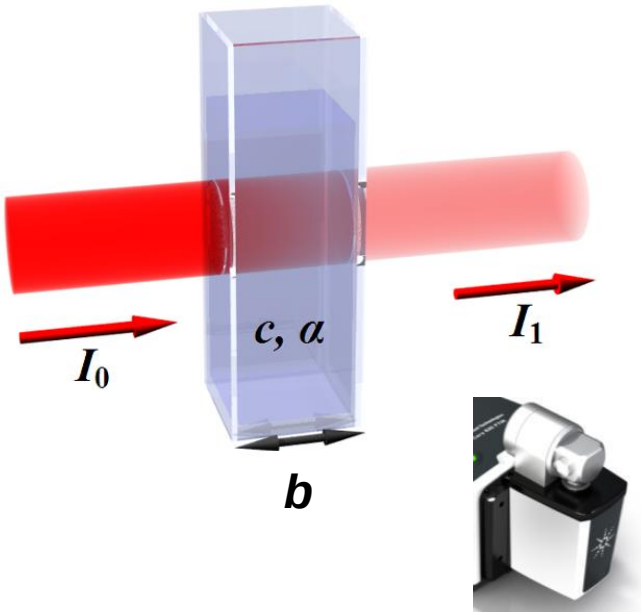


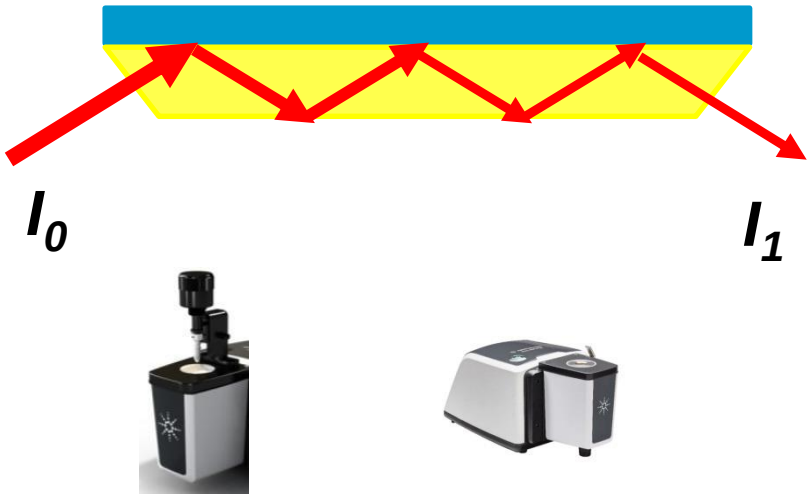
Soft Drink Sample using 10 Reflection and 1 Reflection ATR

- 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

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.

Transmission vs. ATR

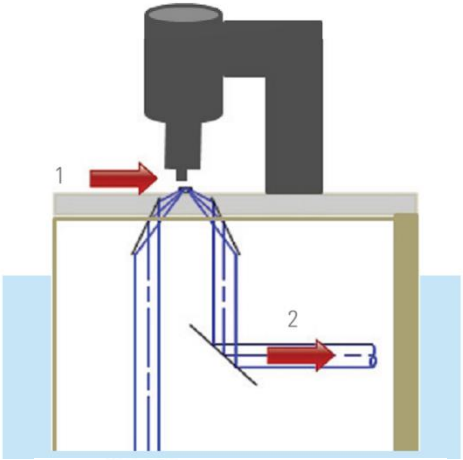
- Both Transmission and ATR can be used to study liquid samples, but they have clear differences.
- Transmission is a bulk testing and ATR is a surface testing (small penetration depth). Same results are expected only for homogeneous samples (e.g. a pure solvent or a stable solution).
- Different quantitation 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)

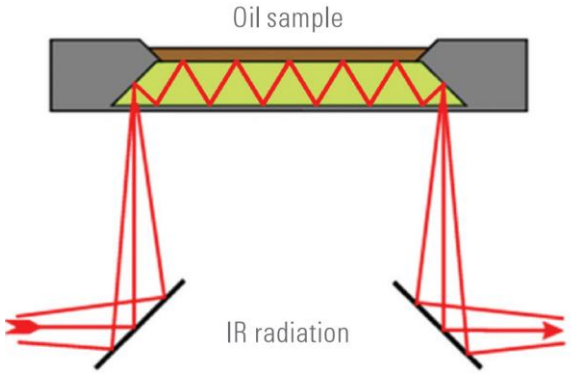
Cary 630 Attachments for Petroleum Product Analysis

- **Single Bounce ATR**: Diamond-based and Ge-based, Pathlength 0.5-2um, for Liquid, Grease and Solid, for both qualification and quantification.
- **Multiple Bounce ATR**: ZnSe-based, pathlength 5-10um, mainly for Liquid quantification.
- **Transmission Cell**: Dialpath and TumblIR, pathlength 30-2000um, mainly for Liquid quantification.

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.



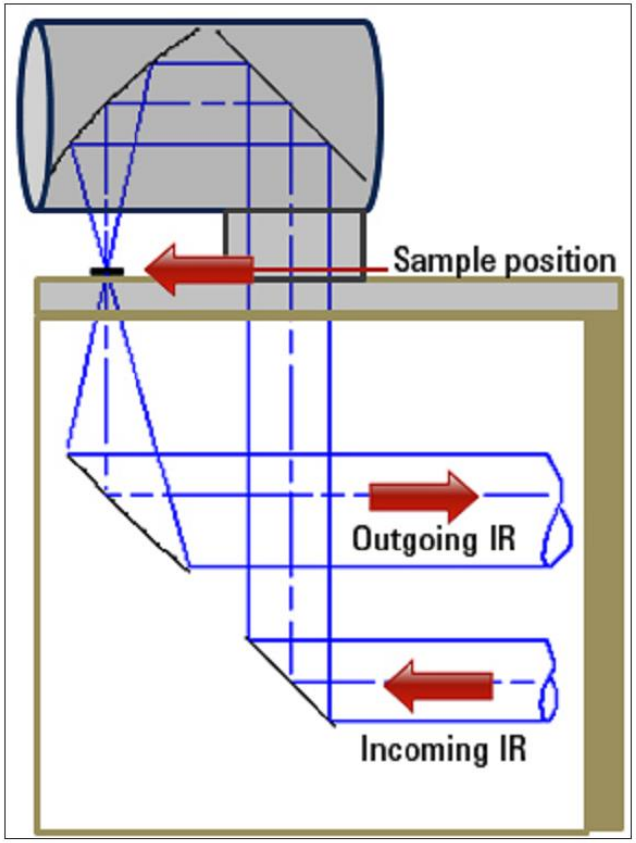


Multiple-Bounce ATR provided greater absorption than single-bounce ATR and a easier sample handling than Dialpath. A very useful technology to test liquid samples.

Single Bounce

Multiple Bounce

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

Crude Oil FTIR Analysis

- Crude oil usually require fast onsite analysis to characterize the compositions.
- Crude oil samples are black viscous liquids with strong IR absorption, making ATR the best approach.
- Cleaning is the most challenging step, usually requiring tissue wiping and solvent cleaning.
- Diamond-ATR is preferred due to higher chemical resistance. Ge-ATR is only considered when the absorption is too strong.

Light Fuel Oil FTIR Analysis

- Light Fuel Oils (i.e. Gasoline, Kerosene and Diesel) are usually homogeneous volatile liquid
- For fast ID, Grading, Anti-adulteration and for certain components (i.e. ethanol concentration), Diamond-ATR is enough
- For more accurate and sensitive quantitation such as Octane rating, antioxidant and additives, Multiple-bouncing ATR or transmission attachment would be needed
- Light fuel cleaning is NOT difficult, their volatility makes them “self-cleaning”.
- Tissue wiping can speed up the cleaning.

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Heavy Fuel Oil FTIR Analysis

- Heavy fuel oil samples are usually high viscous liquid, similar to crude oil.
- The testing technique is similar to crude oil, Diamond-ATR is the preferred technique for most of the analysis due to the convenience and easier cleaning.
- If more accurate and sensitive testing (such as asphaltene quantitation*), a multiple-bounce ATR might be needed since longer pathlength can be achieved.
- Transmission cell wont bring too much advantages and the cleaning is more time consuming than ATR.
- Sample removal would need tissue wiping and solvent cleaning.

* http://dx.doi.org/10.1016/j.forsciint.2016.07.018

Lubricant Oil FTIR Analysis

Common Oil Parameters by FTIR

Parameter	Frequency (cm^{-1})	Traditional Method
Oxidation	1710	Acid number (AN) titration
Nitration	1630	None
Sulfation	1150	Base Number (BN) titration
Diesel Fuel	810	Flash Point, Gas Chromatography
Gasoline	750	Flash Point, GC
Water	3420	Karl Fisher
Glycol	1080,1040, 880	Colorimetry, GC
Soot	2000	Thermogravimetric
Antiwear	980	Elemental Analysis (Zn etc.)
(T)BN	1516,1152	BN by titration

➢There are massive needs for lubricant quality monitoring because it is a critical condition to maintain machine operation. FTIR spectroscopy has been accepted as industrial standard for lubricant analysis, due to its speed, sensitivity, multiple and affordability.

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Lubricant Oil FTIR Analysis

- Virgin lubricant oils are high viscous non-volatile liquid. Different type of additives are added on purpose to adjust the performance.
- Additives include anti-wear, anti-oxidant viscosity modifier and so on, they may have significantly different concentrations.
- During usage, degradation, contamination and additive consummation would cause subtle compositional changes, which can be detected by FTIR spectrometry.
- The used lubricant oil could have increased viscosity and heavy contamination, making the cleaning more challenging.

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Lubricant Oil FTIR Analysis

- Spectral features from additives are usually weak, requiring large pathlength.

Pathlength (µm)	Typical Conc. Range
30	Neat - 0.1%
50	50% - 500 ppm
100	20% - 100 ppm
200	10 % - 50 ppm

- The multiple components could change at the same time, requiring Chemometric algorithms to achieve multiple component analysis
- Thorough cleaning is critical to avoid cross-contamination and is usually the speed limit for batch testing..

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Grease FTIR Analysis

- Grease are high viscous gel-type materials, usually more difficult to remove.
- Single-bounce Diamond-ATR is mostly used due to its convenience.
- Grease removing need both solvent washing and tissue wiping.
- Fresh background would be needed for each sample.
- If transmission cell has to be used (e.g. low level components), it is critical to remove bubbles to ensure constant pathlength.

Asphalt FTIR Analysis

- Asphalt samples are solid or gel or liquid-like materials (depending on temperature). The black sample have high IR absorption.
- The most critical challenge is to protect window materials from asphalt, which is extremely difficult to remove.
- Asphalt removing need both special remover (e.g. α-Limonene), “violent” wiping and even scraping might be also needed.
- Diamond-ATR is the most preferred technique, because it is hard enough to survive the harsh cleaning process.

Asphalt FTIR Analysis

- Asphalt sample are usually non-uniform, replicated measurements are needed.
- Even though Ge-ATR may help to yield less interfered spectra. It is usually not recommended because it is soft and thus vulnerable during cleaning.
- If transmission techniques have to be used. Asphalt sample are usually made into thin slices (by heating, pressing, cooling and cutting) and sandwiched in KBr pallets.
- Anytime, direct contact between Asphalt and reusable IR transmission windows must be avoided

Lab Testing vs. Field testing

Lab Testing

Field Testing

- Lab testing yield more comprehensive results testing (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 problem. For example, crude oil field analysis can help well drilling significantly.
- Agilent has solution for both.

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Summary

- Petroleum Products are a group representative samples, which require proper selection of FTIR testing techniques.

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

    - Easiness of operation
    - Sensitivity and pathlength
    - Protection of the window

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

QUESTIONS?