Innovative Leaps in FTIR Technology
Introducing the next generation of handheld FTIR for non-destructive analysis

Presenter:
Shannon Richard, Product Manager
Mobile Measurement FTIR Products
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More than 60 years of identifying and confirming both target and unknown molecules

1947
First commercial recording UV-Vis, the Cary 11 UV-Vis

1954
Release of the Cary 14 UV-Vis-NIR

1969
First rapid-scanning Fourier transform infrared spectrometer, the FTS-14

1979
First use of a mercury cadmium telluride (MCT) detector in a FTIR

1982
First FTIR microscope, the UMA 100

1989
Release of the acclaimed Cary 1 and 3 UV-Vis

1999
First 256 x 256 MCT focal plane array for analytical spectroscopy

2000
First ATR chemical imaging system

2007
Smallest, most rugged commercially available interferometer introduced

2007
TumBlIR sample accessory introduced – a revolution in FTIR liquid sampling

2008
First handheld FTIR, the ExoScan

2011
The Cary 630 FTIR raises the bar for routine analysis of solids, liquids, and gases

2014: Next-generation, 4300 Handheld FTIR introduced

Agilent Technologies

Confidentiality Label
February 3, 2015
Agilent’s FTIR Family

Agilent has the widest range of FTIR instruments – from Mobile to Routine to Research to Microscopy
RELIABLE: “From white coats to work boots”
When does NDT happen?

- Articles too big or too expensive to take a sample
  - Aerospace, automotive, building materials
  - Solar panels, wind turbines, large composite parts
- Historical objects, art
- Damage analysis
- Surface Cleanliness
- Material Identification
- Not just first article… every article
- Material or coating performance
- Real world measurement

Efficient Field Sampling

- Geology, soil science
- Efficiently “map” out areas
- “Ground truthing”, contamination, nutrient distribution

“Many times, taking a sample to the “lab” isn’t an option”
Agilent’s 4300 Handheld FTIR
Innovations for NDT Environments

Innovative Optical Design
- All Components Optimized for throughput
- Measurements taken in any direction
- No Alignment needed
- Utilizes ZnSe optics to withstand environmental conditions
- True Michelson Interferometer ensures full wavenumber range capabilities (DTGS Detector)
- First handheld system to employ a TE controlled MCT detector for higher sensitivity applications
Innovative Ergonomic Enhancements

- **Weight** — the 4300 is the lightest handheld FTIR system currently available (2.2 kg).
- **Center of gravity** — The center of gravity of the 4300 Handheld FTIR is exactly in the middle of the handle and at the trigger.
- **Control Trigger** — The single control trigger is located where the index finger naturally falls when holding the system.
- **User screen** — The screen is articulated and is easily read regardless of the position of the 4300 Handheld FTIR or amount of ambient light present.
- **Sample interface selection** — Changing the sample interface is a simple one hand operation that takes seconds to accomplish.
Innovative Field Readiness

- Interfaces to meet a wide range of complex sampling needs*
- Simple one-handed action changes sampling interface
- No alignment necessary, can only be installed one way
- RFID tagged to customize methods to specific sampling interfaces
- Capability of “hot swapping” batteries for extended field use

* Diamond ATR, GE ATR, External Reflectance, Grazing Angle, Diffuse reflectance
HANDHELD FTIR APPLICATION

Effect of Ergonomics on Data Acquisition and Reproducibility
Handheld FTIR Application
Designing an experiment to show the benefits of better ergonomics

Hypothesis
• A lighter weight system is preferred over a heavier one, however, the center of gravity of the system must be optimized as well.
• If the spectrometer’s center of gravity is located above the hand that is holding it, muscles will tire even more rapidly, resulting in unwanted movement that affects data quality.
• In contrast, a system with a properly positioned center of gravity causes less strain and less potential for movement during data acquisition.
Handheld FTIR Application
Ergonomics - Methodology

• The 4100 Exoscan system weighs 1 kg (2.2 lbs) more than the 4300 Handheld FTIR system and the center of gravity of the older system is located approximately 10 cm (2.5 in) above the supporting handle.

• The data set for this study was collected from a series of coatings used in a composite aerospace application. The coating was comprised of six distinct samples.

• An experienced technician made all the measurements; the height of the samples required measurement with an outstretched arm.

• Even at the short 8 second collection times, the positive effects of greater ergonomics can be observed.
Comparison between handheld data of an epoxy resin sample collected on the 4100 ExoScan (red) and the new 4300 Handheld FTIR (blue) with improved ergonomics. The 4300 Handheld FTIR spectrum has less baseline noise and greater band definition due to the user’s ability to hold the instrument steady, even during an overhead measurement.
Comparison calculating RMS noise using:

- The RMS noise was measured in the region from 2750–2550 cm\(^{-1}\). This region contains no spectral bands.
- Using the external reflectance sample interface, the amount of light falling on the detector (and therefore the baseline noise) is directly correlated to accuracy of sample focus.
- The average baseline noise in the 4300 Handheld FTIR measurements is 35% lower than the 4100 ExoScan measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>4100 Baseline Noise</th>
<th>4300 Baseline Noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Resin</td>
<td>0.00197</td>
<td>0.00133</td>
</tr>
<tr>
<td></td>
<td>0.00316</td>
<td>0.00165</td>
</tr>
<tr>
<td></td>
<td>0.00240</td>
<td>0.00145</td>
</tr>
<tr>
<td>Primer</td>
<td>0.00196</td>
<td>0.00084</td>
</tr>
<tr>
<td></td>
<td>0.00199</td>
<td>0.00063</td>
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<tr>
<td></td>
<td>0.00157</td>
<td>0.00066</td>
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<tr>
<td>Basecoat</td>
<td>0.00252</td>
<td>0.00281</td>
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<td></td>
<td>0.00297</td>
<td>0.00269</td>
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<tr>
<td></td>
<td>0.00242</td>
<td>0.00262</td>
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<tr>
<td>Topcoat 1</td>
<td>0.00160</td>
<td>0.00080</td>
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<tr>
<td></td>
<td>0.00155</td>
<td>0.00080</td>
</tr>
<tr>
<td></td>
<td>0.00165</td>
<td>0.00099</td>
</tr>
<tr>
<td>Topcoat 2</td>
<td>0.00150</td>
<td>0.00093</td>
</tr>
<tr>
<td></td>
<td>0.00155</td>
<td>0.00097</td>
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<tr>
<td></td>
<td>0.00155</td>
<td>0.00081</td>
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<tr>
<td>Topcoat 3</td>
<td>0.00183</td>
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<td></td>
<td>0.00164</td>
<td>0.00063</td>
</tr>
<tr>
<td></td>
<td>0.00137</td>
<td>0.00119</td>
</tr>
<tr>
<td>Average Noise</td>
<td>0.00196</td>
<td>0.00126</td>
</tr>
</tbody>
</table>
Library comparison also shows superior performance for the 4300 Handheld FTIR. Since the libraries used in this comparison were developed individually on each instrument, correlation values less than ideal (R-1=1.0) are due to instability in sample focus. The results of the library experiment are tabulated in Table 1.

- In 14 out of 18 samples, the handheld data collected on the 4300 Handheld FTIR had a higher correlation than data for the same sample collected on the 4100 ExoScan.
- The average correlation value for the 4300 Handheld FTIR was higher than the average value for the 4100 ExoScan.
- The standard deviation in correlation values for the 4300 Handheld FTIR was half that of the 4100 ExoScan, demonstrating that the increased ergonomics of the 4300 handheld FTIR allows for more consistent, reproducible measurement.
HANDHELD FTIR APPLICATION

Positive Material Identification
Handheld FTIR Application
Positive Material Identification (PMI)

Need for measurement

– Insure correct material prior to usage
– Labeled correctly, meets specification, will perform as designed
– Common with metal alloys …

Polymers, plastics, elastomers, composites and coatings

– PMI required for these as well
  – Incorrect materials could cause catastrophic failure
– XRF unsuitable
– FTIR uniquely suited for these materials

Tailor measurement for analysis needs

– Material ID
– Counterfeit ID, Quality Assurance
– Measure to specification, Presence or absence of material
Handheld FTIR Application

PMI- Analytical Techniques

Library Search
- Library comprised of single samples
- Correlation between sample and each entry calculated
  - Ranked to show best match
- Good for large number of possibilities
  - 5 – 10% minimum detectable difference

Discriminant Analysis
- Multiple spectra used for each class
  - Use PCA or PLS to find commonality
- Use a statistical measure to determine if in group
- Good for a fixed set of possibilities
  - 1 – 5% minimum detectable difference

Qualification using Quantitation
- Measure amount of known ingredient or contaminant
- Use presence/absence to qualify material
- Highest level of confidence
  - 0.1% minimum detectable difference

\[ R = \frac{\sum_{i=1}^{n} T_i R_i}{\left( \sum_{i=1}^{n} T_i^2 \right)^{\frac{1}{2}} \left( \sum_{i=1}^{n} R_i^2 \right)^{\frac{1}{2}}} \]
Handheld FTIR Application
PMI – Identification

Easy to use, simple to implement
– Often, only a basic identification is required
– “Is this nylon or polystyrene?”
– Large number of materials or possibilities

Libraries
– Commercially available
– Self generated
  – Easy to use software for library generation

Handheld measurement using ATR
– High correlations (> 0.9) with correct match
– Can identify material even if it’s not correct
The 4300 Handheld FTIR system used to identify scrap polymer material sourced from electronics equipment.

- Diamond ATR interface – features a novel spherical diamond sensor
- Identified polymer using MicroLab software and polymer libraries
- The spectrum and identity of the unknown polymer sample is provided, as well as the spectrum of its best library match and a numerical value that reflects the quality of that match
Sometimes, more information is needed
– Confirm identity to a higher degree of certainty
– Differentiate between samples which are chemically close

Fundamentally a different question
– “Is this material X… yes or no?”

Discriminant Analysis puts a statistical measure on ID
– Able to answer Yes/No with a known error
  – More confidence in the answer
Discriminant models were created to identify two different types of seals which are used in the petroleum industry.

- The first calibration predicts VMQ 01 (silicone) type o-rings
- The second group predicts FKM type 1 o-rings
- Both models were made using a partial least squares discriminant analysis (PLS-DA) technique
- A single calibration set was collected for both methods
- The calibration set is comprised of 10 or more samples each of 18 different elastomers, resulting in a total of 275 spectra
- For each calibration, values were assigned to the spectra; a value of “0” was given to the target group, while the non-target samples were given higher values
Classification of VMQ elastomers

- The model uses mean centering, area normalization, and a 9-point Savisky-Golay first derivative as preprocessing and 6 factors. As shown in the figure, the data set is clearly divided into two groups.
- A threshold can be set on the PLS value which clearly distinguishes VMQ o-rings from others.
Handheld FTIR Application

PMI - Verification

Specification Verification via Discriminant Analysis

- 8 different categories of FKM materials
  - Similar Formulations
  - Unique Properties based on Formulation
- Target group FKM Type 1
  - FKM T1 = 1
  - All others = 10
- Samples which had greater chemical differences, such as nitrile rubber, hydrogenated butadiene rubber, EPDM and chloroprene were given a value of 15
- Finally, samples which were very different, such as dimethyl siloxanes (PDMS) and fluorinated PDMS, were given a value of 20.

- This range of values allowed the model to accurately distinguish FKM Type 1 from other FKM types from other kinds of elastomers.
The classification results using cross validation are shown in Figure 7. Similar to the previous method, the data was preprocessed by mean centering, area normalization and a 9 point Savisky-Golay first derivative. Seven factors were used in this method.
HANDHELD FTIR APPLICATION

Quality Control
Adhesive bonding dependent on surface prep

- Stronger than mechanical, IF prepared properly
  - Difficulty measuring prepared bonds
- Measurement before bonding required

Plasma treatment

- Cleans surface prior to bonding
  - Removes mold release from peal-ply
- Distance / Temperature variances cause over / under treatment

Calibration developed for plasma treatment distance

- Both wax and silicone based mold release calibrated
  - 2 separate methods
- Verify correct treatment performed
Handheld FTIR Application

Quality Control

Plasma treatment

- Ramped plasma torch low – high
- Several samples cut, bonded and tested with G1C
- Optimum distance determined
Verification of surface preparation pre-bonding
HANDHELD FTIR APPLICATION

Non-Destructive Evaluation of Composite Thermal Damage
Handheld FTIR Application
NDT Composite Thermal Damage

Challenge:
Composite materials can be irreversibly degraded by excessive heat. Heat damage can occur from many sources, such as engine or missile exhaust, electrical fires, or even lightning strikes. Severe thermal damage is often obvious by visual inspection where blistering or delamination is observed. However, longterm moderate heat exposure is much more common and can be just as catastrophic. This type of heat damage is referred to as incipient thermal damage, since the part may have little or no visible damage.

Solution:
Agilent FTIR instruments, including the 4300 Handheld FTIR can be used for detecting thermal damage in composites. This information can be used to define the breadth and depth of a thermally overexposed region of composite to assist in repair procedures.
Handheld FTIR Application

NDT Composite Thermal Damage

Method Develop is based on Individual Composites and specific to those composites

- Partial least squares (PLS) chemometric models are used
- Composite coupons exposed to a range of temperatures (375 to 550°F) are used to “train” the models to detect spectral changes due to thermal damage.
  - Each calibration set consists of composite coupons exposed to 375°F, 400°F, 425°F, 450°F, 475°F, 500°F, 525°F and 550°F temperatures for one hour.
- 8 models have been developed with data collected on the 4300 Handheld FTIR equipped with a diffuse reflectance attachment (4 MCT and 4 DTGS models).
- The spectra are collected at 8 cm⁻¹ resolution and 64 co-added interferograms.

The models are tested using a validation set of composite coupons prepared under similar conditions.
Thermally damaged Epoxy 1 unsanded tape composite material. The composite coupons are exposed to a range of temperatures for 1 hour. The absorbance band at 1722 cm\(^{-1}\) arises from the carbonyl stretch vibration associated with oxidation of the resin and indicates thermal overexposure.

Thermally damaged Epoxy 1 sanded tape composite material. The composite coupons are exposed to a range of temperatures for 1 hour. The 1722 cm\(^{-1}\) vibration is absent in the anaerobic environment.

The decrease in absorbance at 1672 cm\(^{-1}\) provides a good negative correlation to temperature exposure.
## Handheld FTIR Application
### NDT Composite Thermal Damage

### Calibration model performance

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Model statistic</th>
<th>SM905 unsanded</th>
<th>Epoxy 1 tape unsanded</th>
<th>Epoxy 2 fabric unsanded</th>
<th>Epoxy 1 tape sanded</th>
</tr>
</thead>
<tbody>
<tr>
<td>4300 MCT</td>
<td>R²</td>
<td>0.96</td>
<td>0.98</td>
<td>0.97</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>SECV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>8</td>
<td>9</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RMSEP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>14</td>
<td>12</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rel % error</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>3.1</td>
<td>3.0</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>4300 DTGS</td>
<td>R²</td>
<td>0.98</td>
<td>0.98</td>
<td>0.97</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>SECV</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>20</td>
<td></td>
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<tr>
<td></td>
<td>RMSEP</td>
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<tr>
<td></td>
<td>10</td>
<td>10</td>
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<td>Rel % error</td>
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<tr>
<td></td>
<td>1.9</td>
<td>1.8</td>
<td>4.3</td>
<td>4.2</td>
<td></td>
</tr>
</tbody>
</table>
Practical Use

Methods can also measure other aspects of the sample chemistry or the validity of the result. The thermal damage method also identifies whether hydrocarbon contamination is present (oil contamination index) and determines if the sample measurement statistically matches the calibration set (M-distance).

MicroLab results screen from a measurement of a sample of Epoxy 1 Tape unsanded exposed to 500 °F for 60 minutes. The red background shows that this sample exceeds the critical threshold for thermal damage.
Handheld FTIR Materials Measurement

- Verify identity and acceptability of starting materials
- Non-destructively analyze objects where excising samples is not practical
- Identify and obtain more data on most important regions of an object; minimize analysis of less important regions
- Screen material to reduce samples that need to be sent to a lab for additional analysis
- Determine how use affects engineered material performance and lifetime.
- Obtain “real-time” answers that allow actionable decisions to be made on-the-spot
Agilent Mobile Measurement
Lab Quality... When and Where you Need it

- **Eliminate Sample transport time and expense**
- **Rapidly screen and select critical samples**
- **Reduce time to results**
- **Make actionable decisions on-the-spot**
- **Realize productivity gains for finished products**
QUESTIONS? COMMENTS?

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