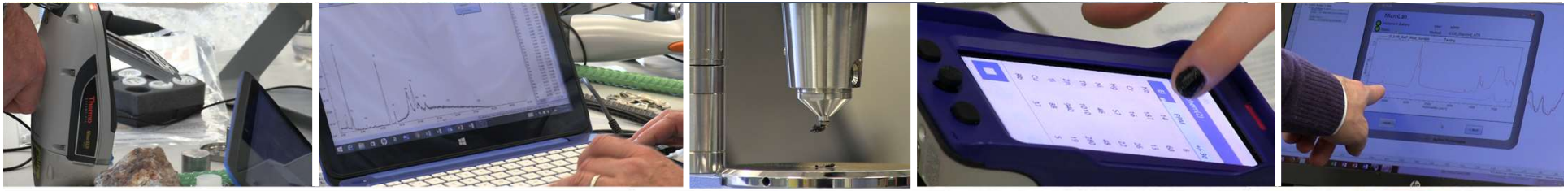


SHRP2 SOLUTIONS
TOOLS FOR THE ROAD AHEAD

Techniques to Fingerprint Construction Materials (R06B)
Fourier Transform Infrared (FTIR) Webinar

Maria Chrysochoou, Associate Professor, University of Connecticut
Derek Nener-Plante, Maine Department of Transportation
Joe Kerstetter, Tennessee Department of Transportation
Cassady Allen, Florida Department of Transportation

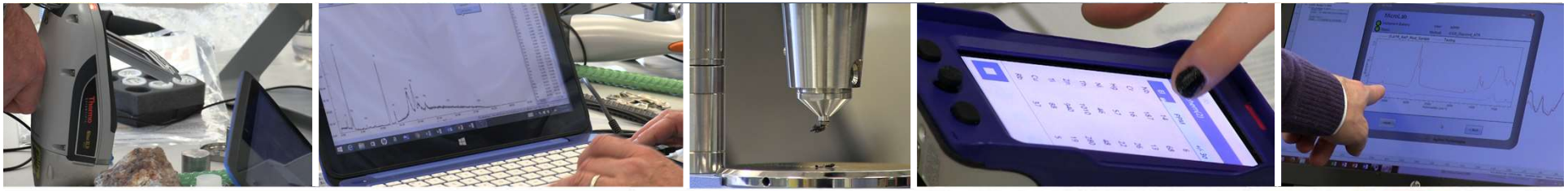
March 27, 2019

U.S. Department of Transportation
Federal Highway Administration

American Association of State Highway and Transportation Officials
AASHTO

Webinar Agenda

- AASHTO Introduction
- FHWA Introduction
- Principles of FTIR – SME
- FTIR applications – Maine DOT
- FTIR applications – Tennessee DOT
- FTIR applications – Florida DOT
- Questions & Answers



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AASHTO Introduction

Kate Kurgan of AASHTO

U.S. Department of Transportation
Federal Highway Administration

American Association of State Highway and Transportation Officials
AASHTO

Focus Areas

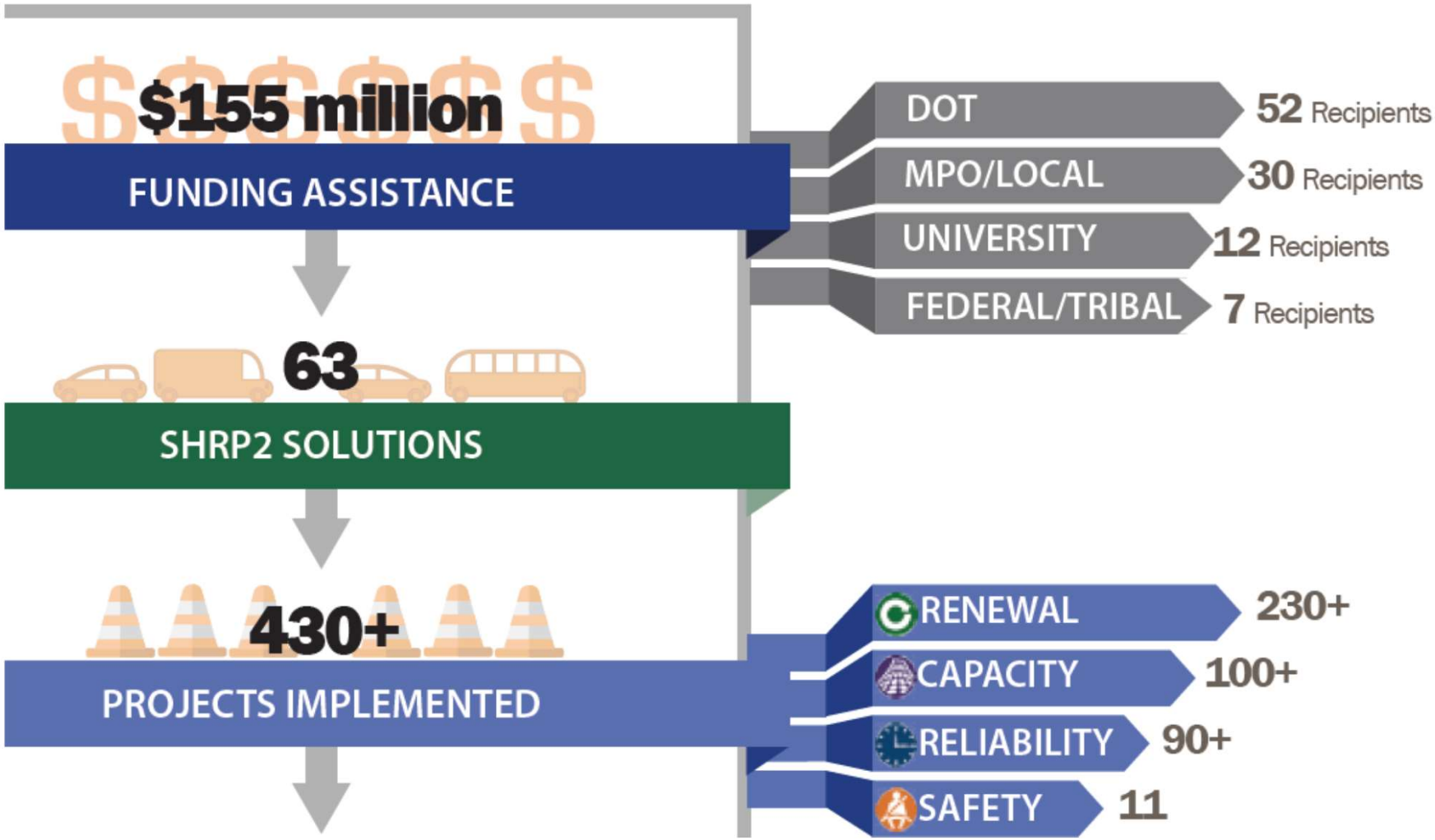
Safety: fostering safer driving through analysis of driver, roadway, and vehicle factors in crashes, near crashes, and ordinary driving

Reliability: reducing congestion and creating more predictable travel times through better operations

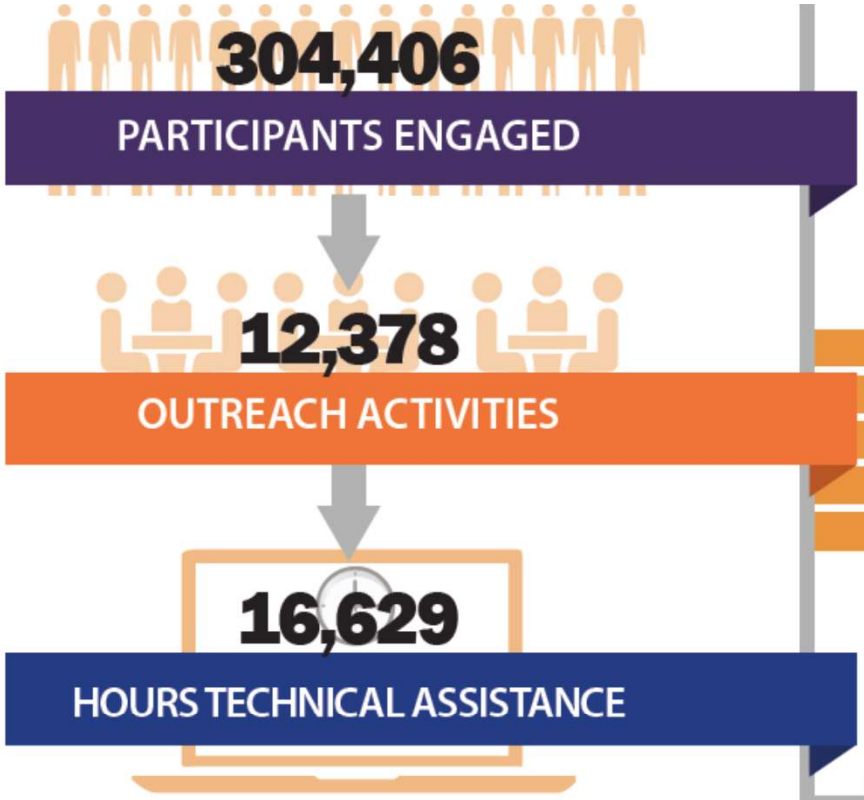
Capacity: planning and designing a highway system that offers minimum disruption and meets the environmental and economic needs of the community

Renewal: rapid maintenance and repair of the deteriorating infrastructure using already-available resources, innovations, and technologies

SHRP2 Implementation:
INNOVATE. IMPLEMENT. IMPROVE.



SHRP2 Implementation:
INNOVATE. IMPLEMENT. IMPROVE.

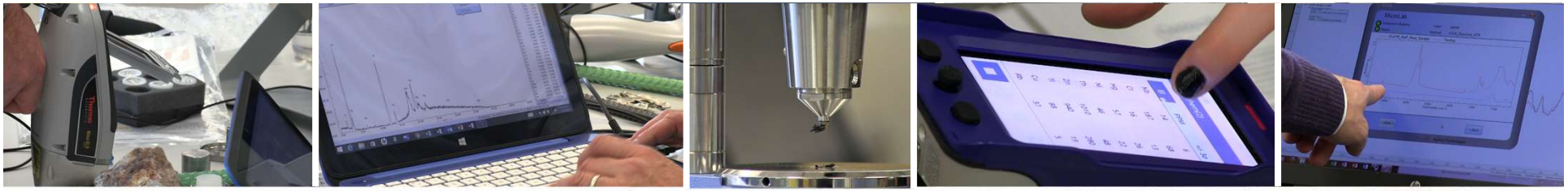


- TRAINING 11,435
- WORKSHOPS 710
- PEER EXCHANGES 106
- DEMOS 76
- SHOWCASES 51

RESULTS

Save lives, money, and time

- Bridges being built more quickly
- Smoother traffic flows and less congestion
- Reduced construction costs
- Safer roadways
- Smarter environmental reviews



SHRP2 SOLUTIONS
TOOLS FOR THE ROAD AHEAD

FHWA Introduction

Steve Cooper of FHWA

U.S. Department of Transportation
Federal Highway Administration

American Association of State Highway and Transportation Officials
AASHTO

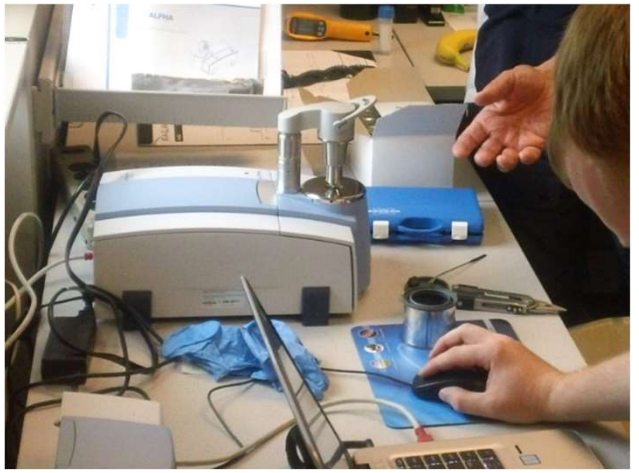
(R06B) Techniques to Fingerprinting Construction Materials

RESEARCH: Explore expanded use of portable spectroscopy technologies in their ability to analyze commonly used construction materials in the field to aid in acceptance.

SOLUTION:

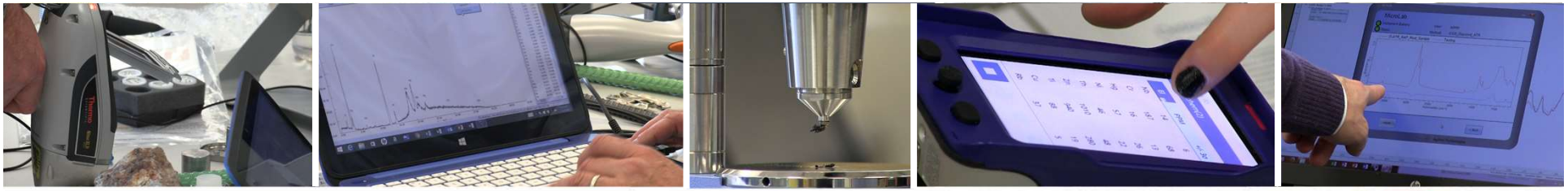
- Summary of Portable Methods & potential use for various materials.
- XRF – For testing pavement markings and epoxy coatings for example.
- FTIR - For evaluating Polymer in HMA, as well fingerprinting admixtures in PCC (accelerators, retarders, curing compounds)
- Generic testing procedures with sampling and data analysis guidelines, as well as proposed standards of practice.

X-Ray Florescence (XRF)



Attenuated Total Reflectance Fourier Transform Infrared (ATR FTIR) Spectroscopy

Portable Spectroscopy Technology



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Principles of FTIR

Maria Chrysochoou, Associate Professor,
University of Connecticut

U.S. Department of Transportation
Federal Highway Administration

American Association of State Highway and Transportation Officials
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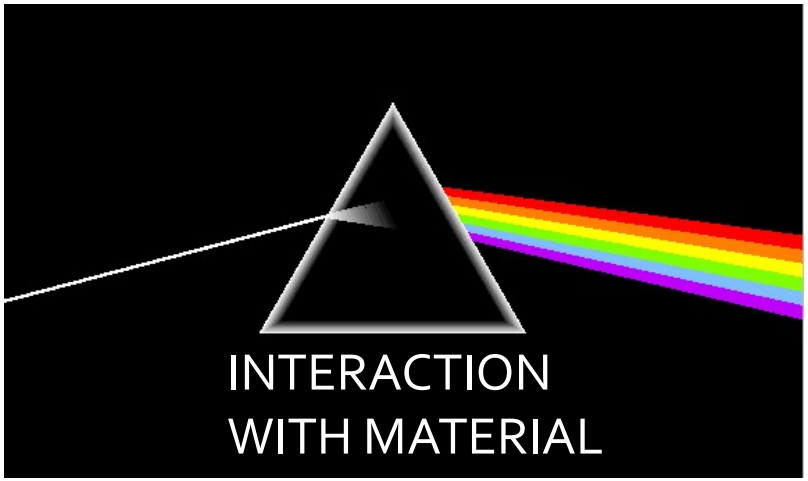
What is spectroscopy?

LIGHT

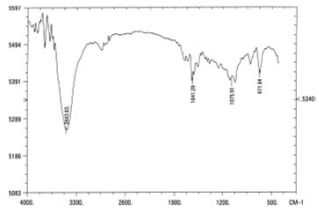


DIFFERENT LIGHT

Radiation source

Material

Detector



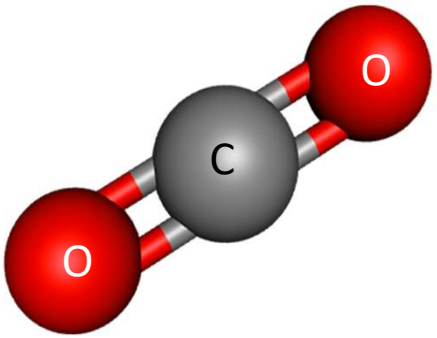
Principle of FTIR

Vibration of asymmetrical molecules happens at characteristic frequencies

Source

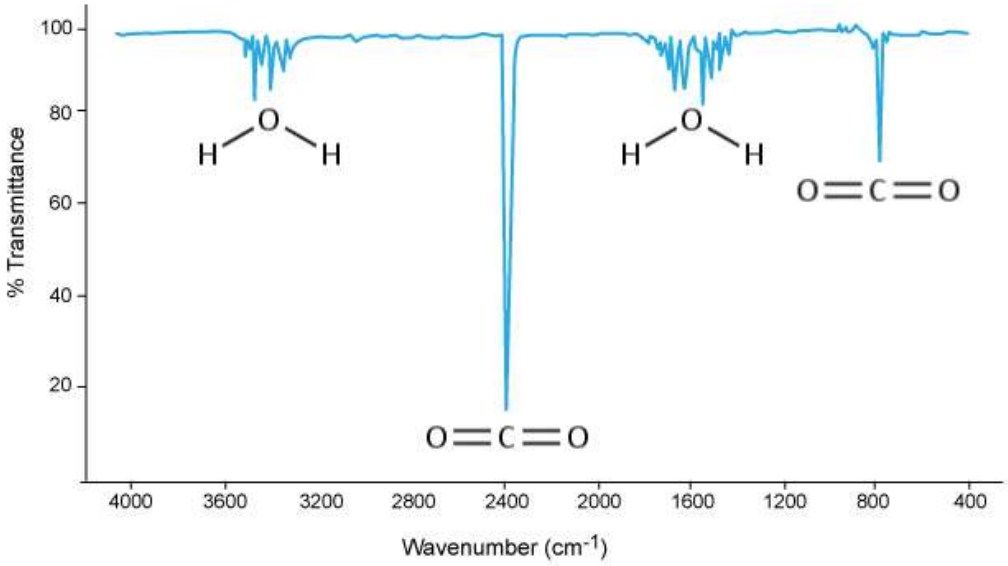
2400 cm^{-1}

1000 cm^{-1}

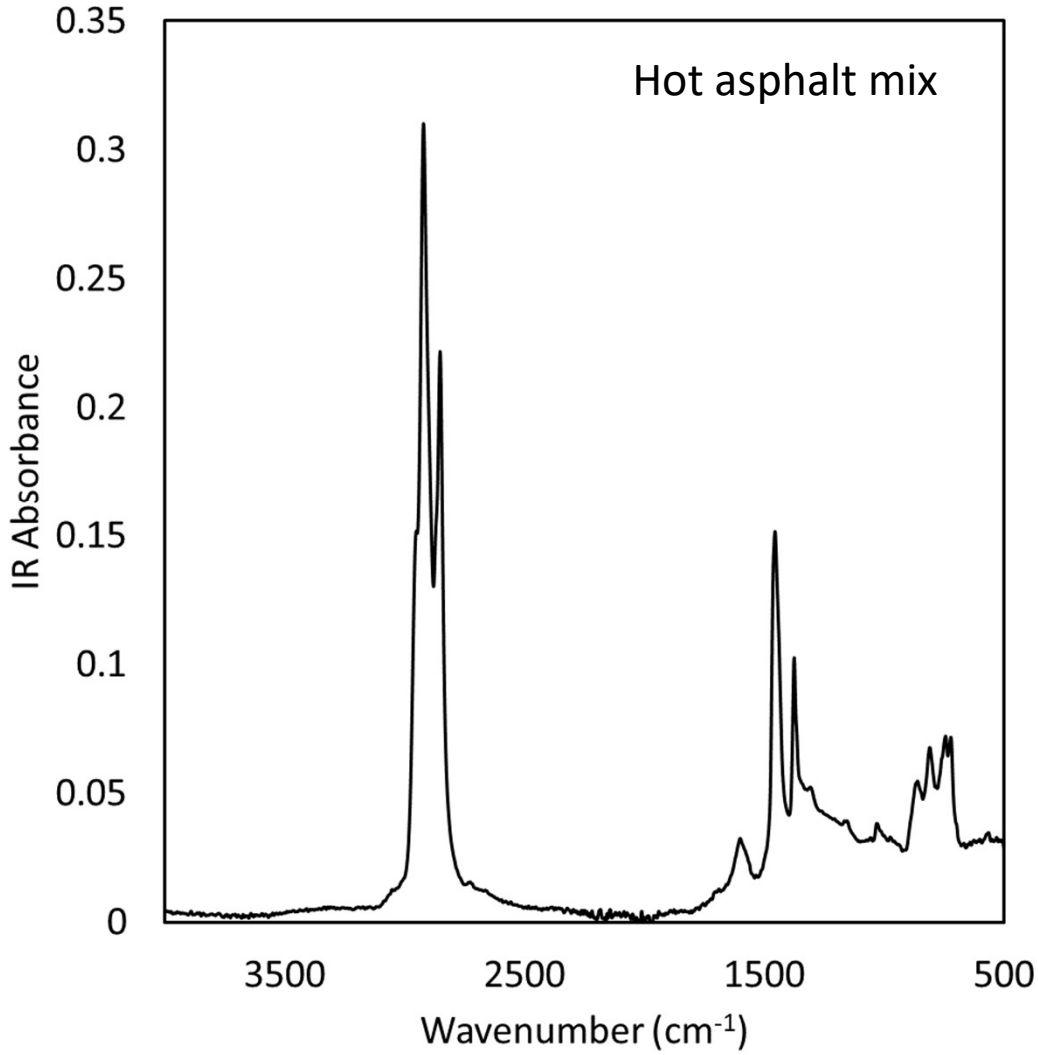


1000 cm^{-1}

Detector



FTIR spectra of complex mixtures



What am I looking at???

Two ways to analyze spectra

Method 1

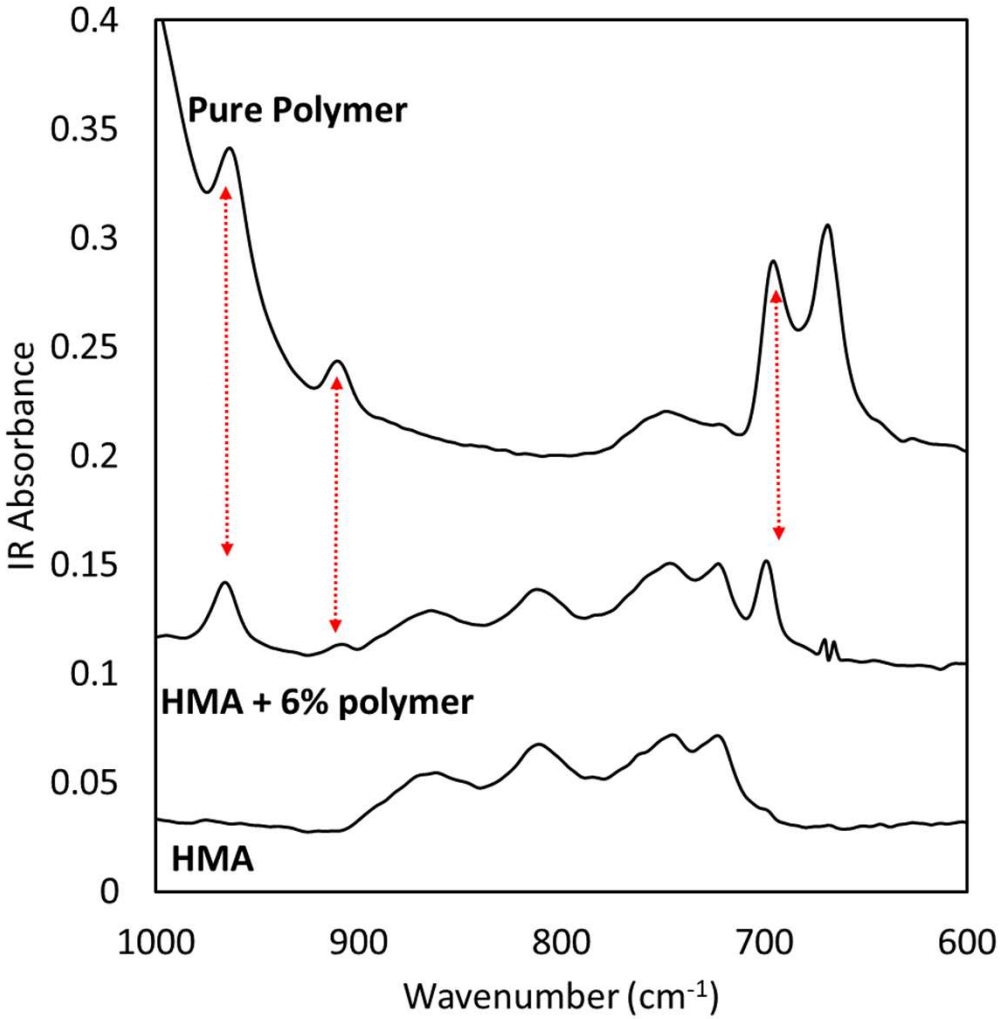
Compare spectrum with spectra of pure compounds and see if peaks match

Method 2

Compare peaks with locations of known functional groups

Method 1: Qualitative Identification of chemical compounds “Fingerprinting”

SBS (poly(styrene-b-butadiene-b-styrene)



You can usually find an admixture if it more than 1%

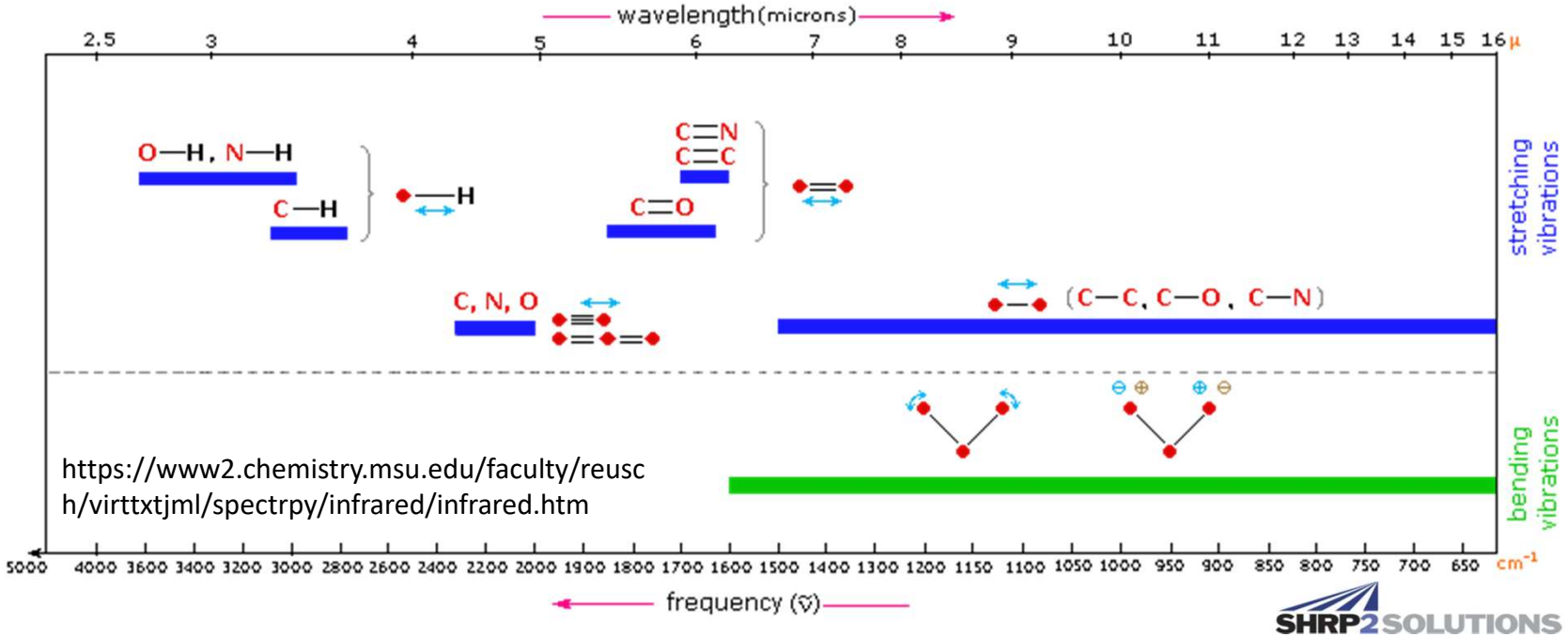
Condition: peaks do not overlap with peaks of substrate

Method 2: Look for characteristic groups

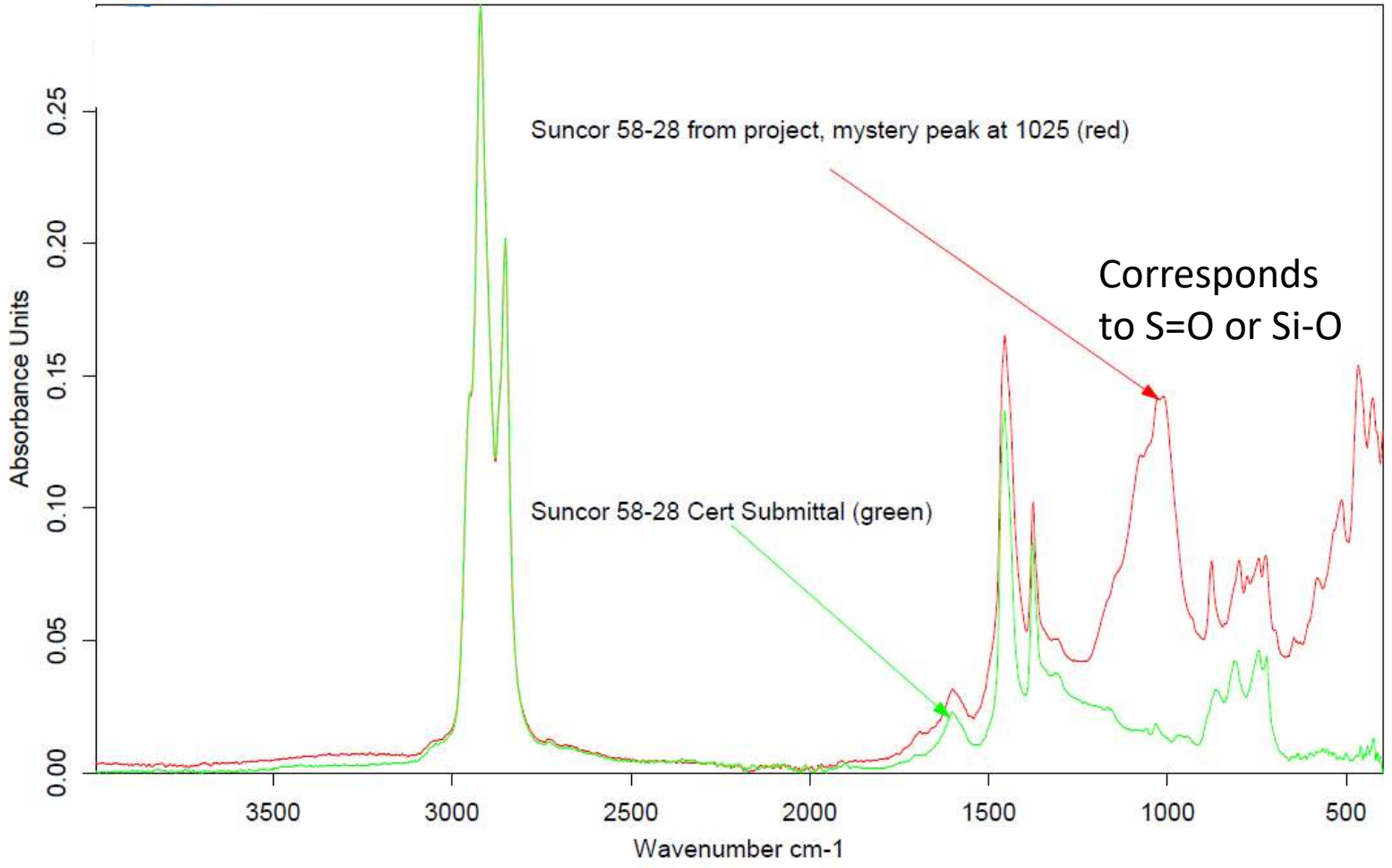
FTIR peaks are a result of the vibration of ***functional groups***, not of entire compounds

These are groups of atoms such as –OH, -S=O, C=C and others, that may combine with each other in infinite ways in complex organic materials

Observing one type of functional group generally does not equal identification of a particular material

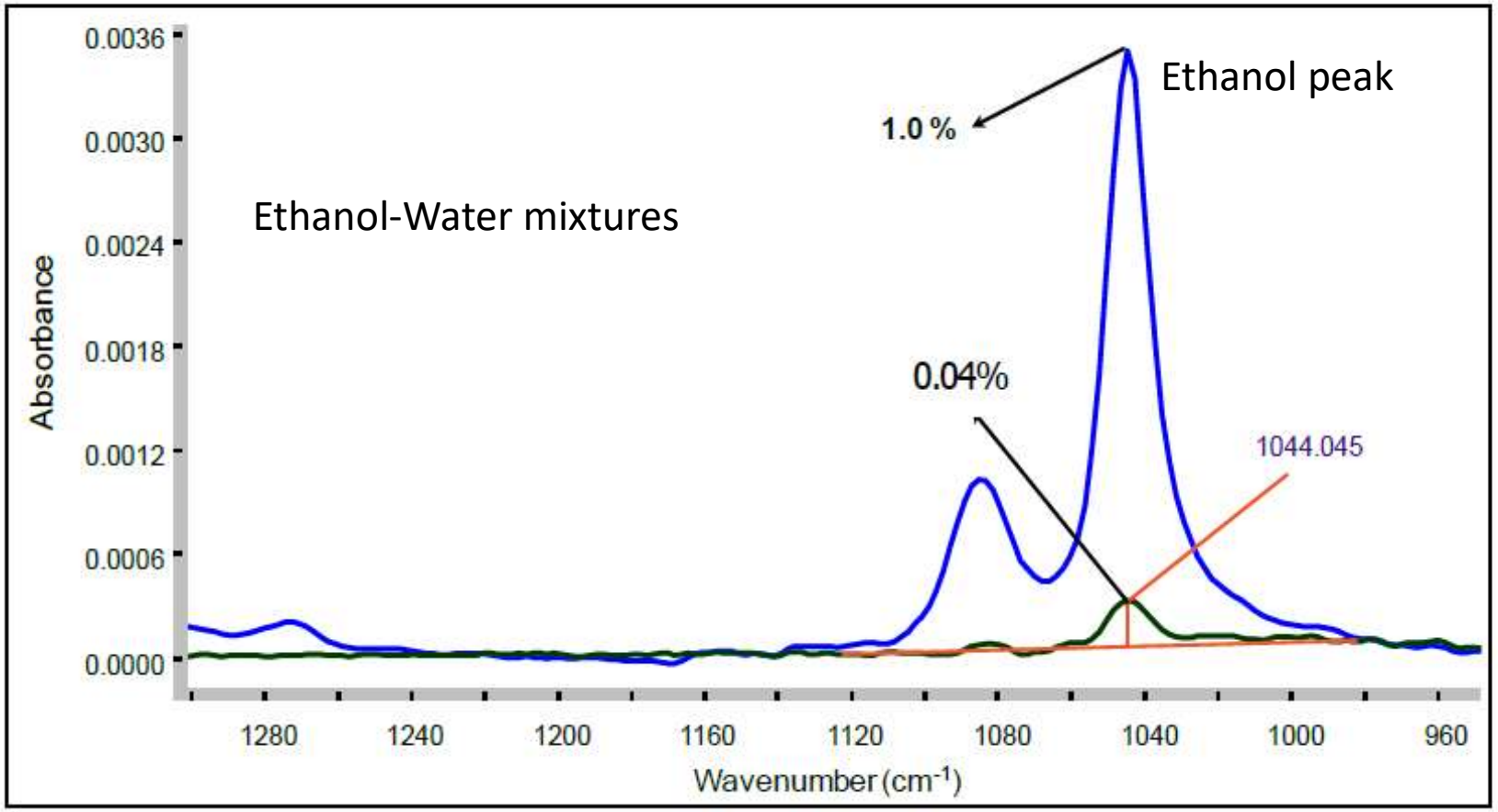


Method 2: Look for characteristic groups – example

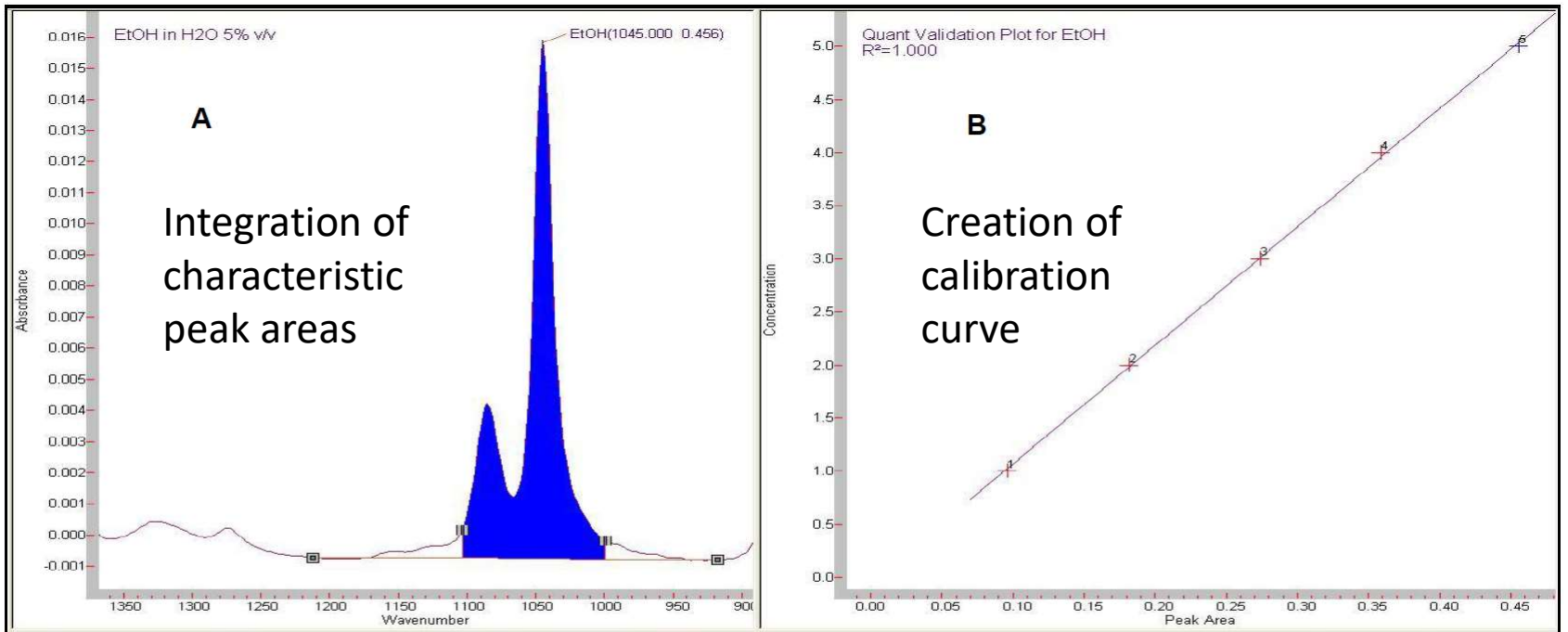


Quantification of chemical compounds using FTIR spectra

Creation of a calibration curve using standard addition of the pure compound



Quantification of chemical compounds using FTIR spectra



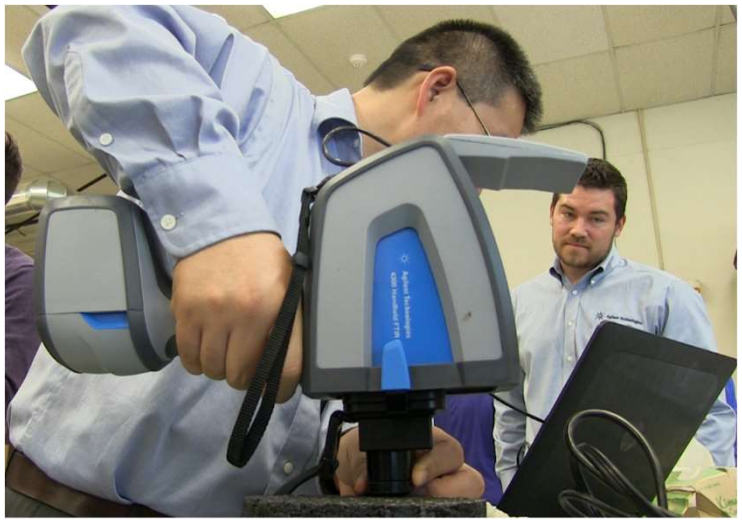
	Name	Spectrum	Include in Quant	EtOH
1	EtOH in H2O 1% v/v		Yes	1
2	EtOH in H2O 2% v/v		Yes	2
3	EtOH in H2O 3% v/v		Yes	3
4	EtOH in H2O 4% v/v		Yes	4
5	EtOH in H2O 5% v/v		Yes	5
6	background (water)		No	

C

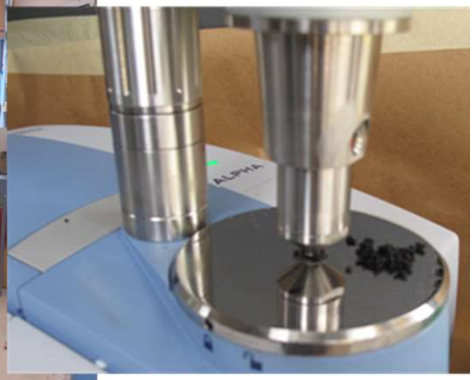
Types of FTIR equipment

Laboratory transmission FTIR
Suitable for gas and liquid analysis, typically not solids

Lab- or field-based Attenuated Total Reflectance (ATR) spectrometer



Diffuse Reflectance (DRIFT) accessory: ATR accessory to probe granular samples



So how do we do it? Some basic tips

- Establishing a library of reference spectra for specific material types is key

- Having a general idea of what it is you are looking for helps

- Use existing databases to narrow down the type of functional group you are looking for

- Use complementary techniques to corroborate your suspicions

Spectral libraries

- Vendors may provide some
- NIST database (16,000 compounds): https://srdata.nist.gov/gateway/gateway?property=IR+spectra and http://webbook.nist.gov/chemistry/vib-ser.html to search by vibration energies
- EPA database (organic contaminants, solvents): https://www3.epa.gov/ttnemc01/ftir/refnam.html
- Free library for organic compounds, searchable by wavenumber: https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi
- Commercial libraries such as http://www.fdmspectra.com/
- Google “FTIR spectra database” and new ones pop up all the time

FTIR Advantages and Limitations

Advantages

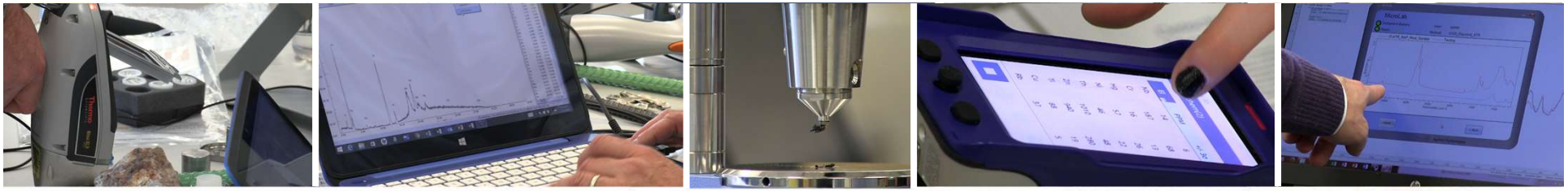
- Little to no sample preparation required (caveat: your job is to make sure sample is representative)
- Actual testing time is 3-5 min.
- Applicable for wide range of materials, including organic materials that are insensitive to X-ray-based methods
- Little maintenance and no operation costs, cost only capital investment

Limitations

- It is only applicable to functional groups that have molecular vibrations in the IR region, i.e. polar, asymmetric, covalent bonds.
- FTIR detects polar functional groups, not entire molecules, and as such the observed peaks are not necessarily unique to a single compound.
- Water molecules have very strong IR active vibrations, which can easily obscure IR active vibrations of other molecules when water presence is substantial, such as in aqueous solutions.
- Interpretation is complicated and requires training

Applications: We will hear from the State DOTs

Maine DOT
Tennessee DOT
Florida DOT



SHRP2 SOLUTIONS
TOOLS FOR THE ROAD AHEAD

Maine DOT

Derek Nener-Plante

U.S. Department of Transportation
Federal Highway Administration

American Association of State Highway and Transportation Officials
AASHTO

R06B–Maine

- MaineDOT goals for R06B:
  - Maximize non-destructive testing
  - Reduce test time and cost
  - Reduce incorporation of out-of-spec material into DOT work
- FTIR
  - Hydrated lime content of asphalt mixture
  - Polymer content of asphalt binder

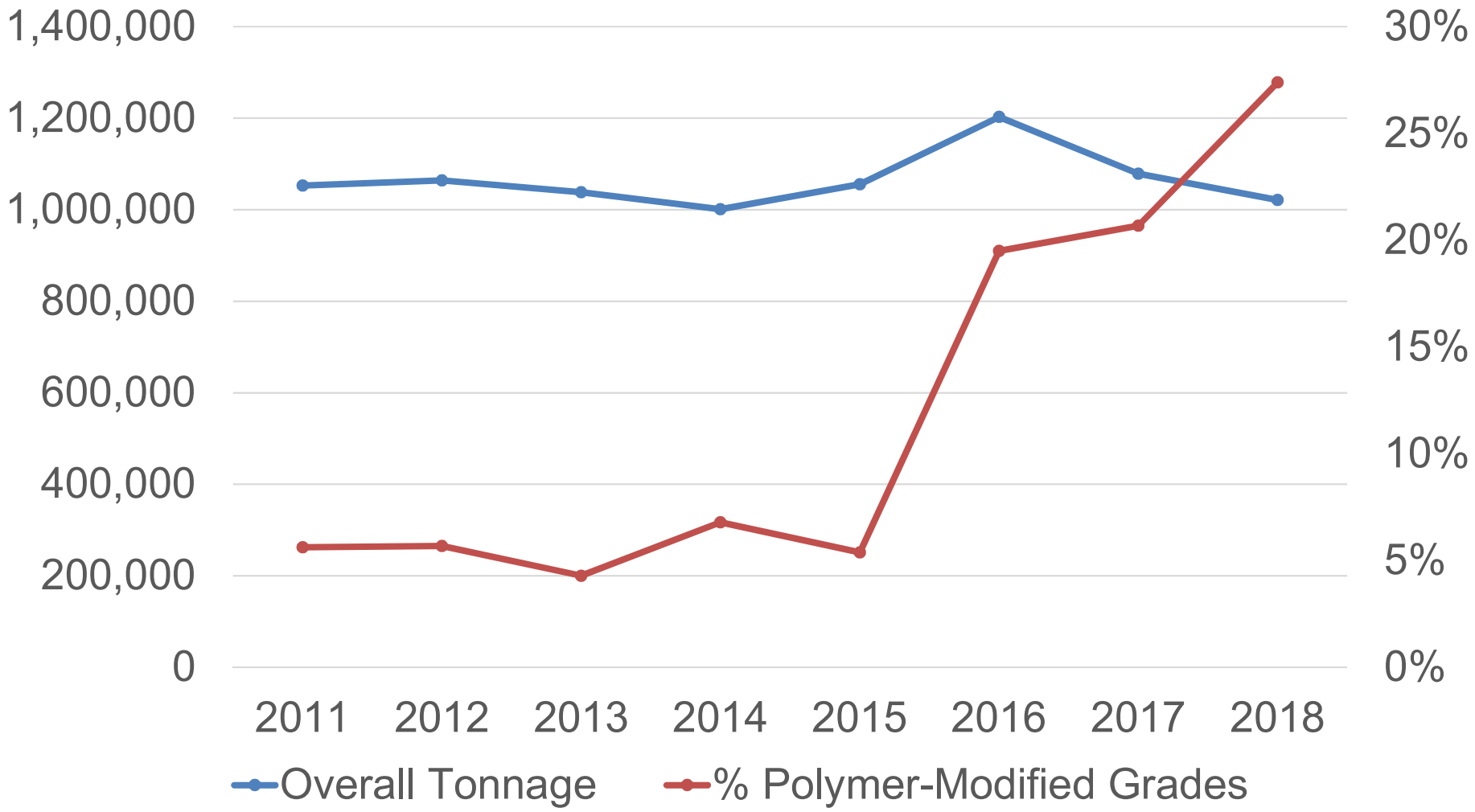
R06B–Maine

- MaineDOT goals for R06B:
  - Maximize non-destructive testing
  - Reduce test time and cost
  - Reduce incorporation of out-of-spec material into DOT work
- FTIR
  - Hydrated lime content of asphalt mixture
  - **Polymer content of asphalt binder**

Maine Polymer Usage – Why?

- Traffic levels are low when compared to others (less than 6 million ESALs)
- Numerous heavy trucks on the system
- Law changed to allow 100,000 lb. loads on Interstate roadways
- Mixture durability issues - raveling and lack of durability
- “If I get one more year in service life, its worth it”

Maine Polymer-Modified Usage



Maine Polymer-Modified Usage

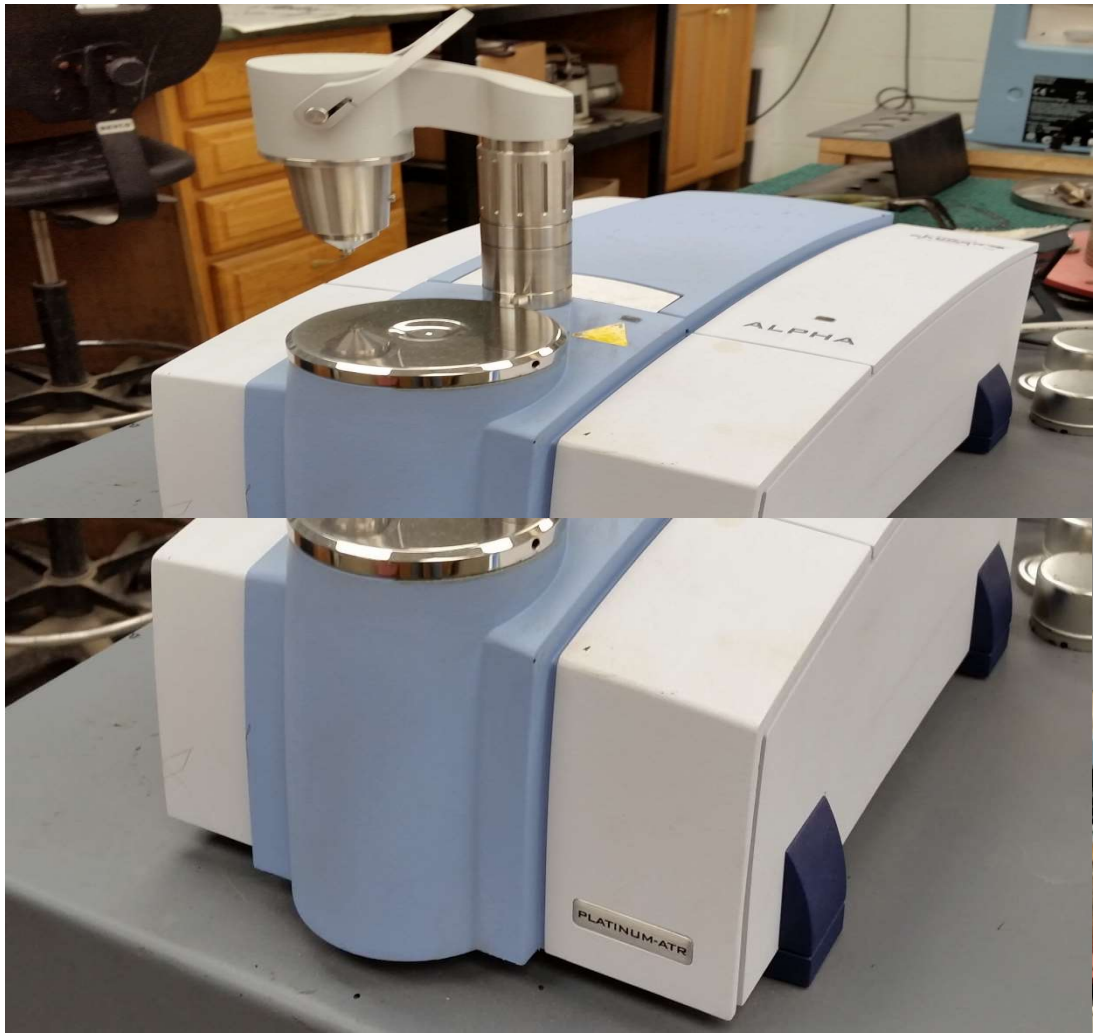
Mix Tons by Year and Grade			
Grade / Year	**2016**	**2017**	**2018**
PG58-28	211,996	132,639	81,180
PG64-28	756,280	723,032	660,454
PG64E-28	231,758	221,185	277,719
PG70E-28	2,772	1,900	2,092

MaineDOT Modified Binder Uses

- Regular Superpave dense-graded mixtures
- Ultra-Thin Bonded Wearing Course – both emulsion and mix
- Porous pavement structures
- High polymer surfaces?

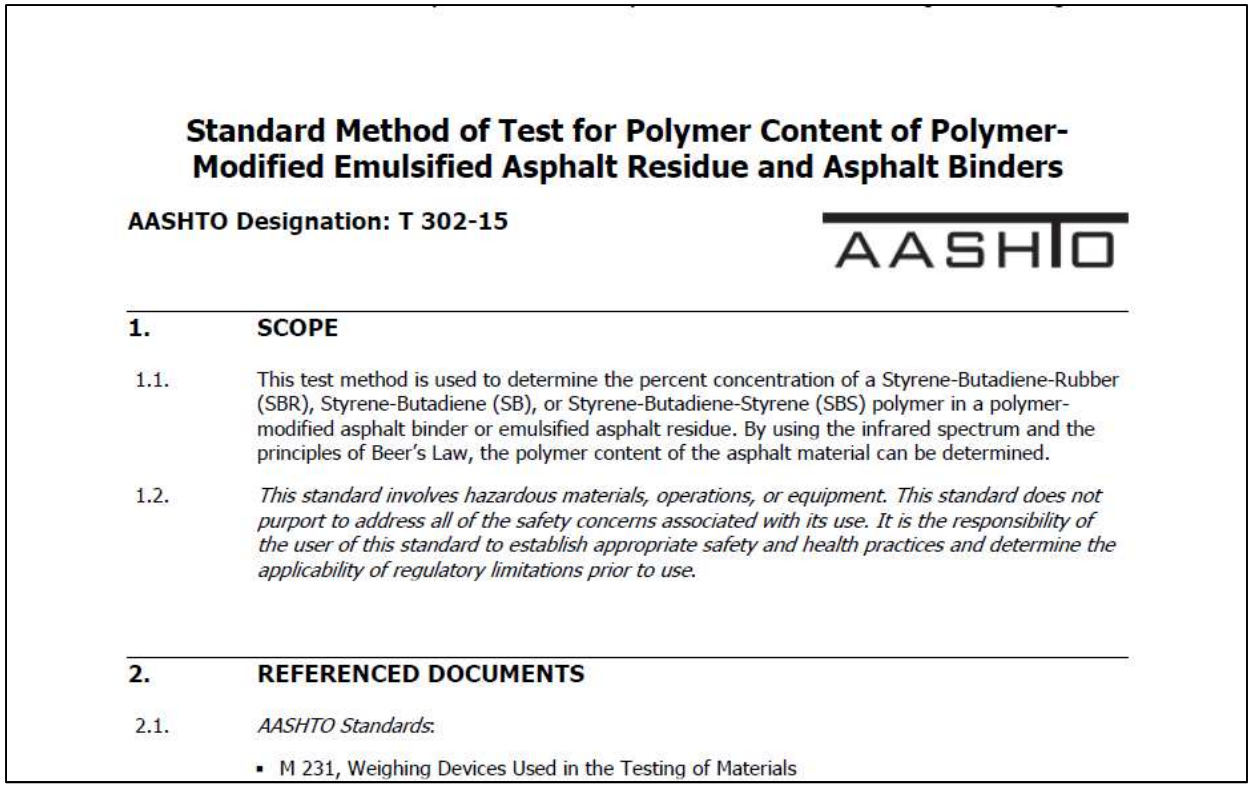
FTIR – Asphalt Binder Samples

- FTIR used on asphalt binder samples taken for verification purposes
- Typically run on unaged asphalt binder
- Sample prep of smearing material over the “window”



FTIR – Asphalt Binder Samples

- FTIR used on asphalt binder samples
- Potential for rapid identification of polymer in asphalt



Standard Method of Test for Polymer Content of Polymer-Modified Emulsified Asphalt Residue and Asphalt Binders

AASHTO Designation: T 302-15

AASHTO

1. SCOPE

1.1. This test method is used to determine the percent concentration of a Styrene-Butadiene-Rubber (SBR), Styrene-Butadiene (SB), or Styrene-Butadiene-Styrene (SBS) polymer in a polymer-modified asphalt binder or emulsified asphalt residue. By using the infrared spectrum and the principles of Beer's Law, the polymer content of the asphalt material can be determined.

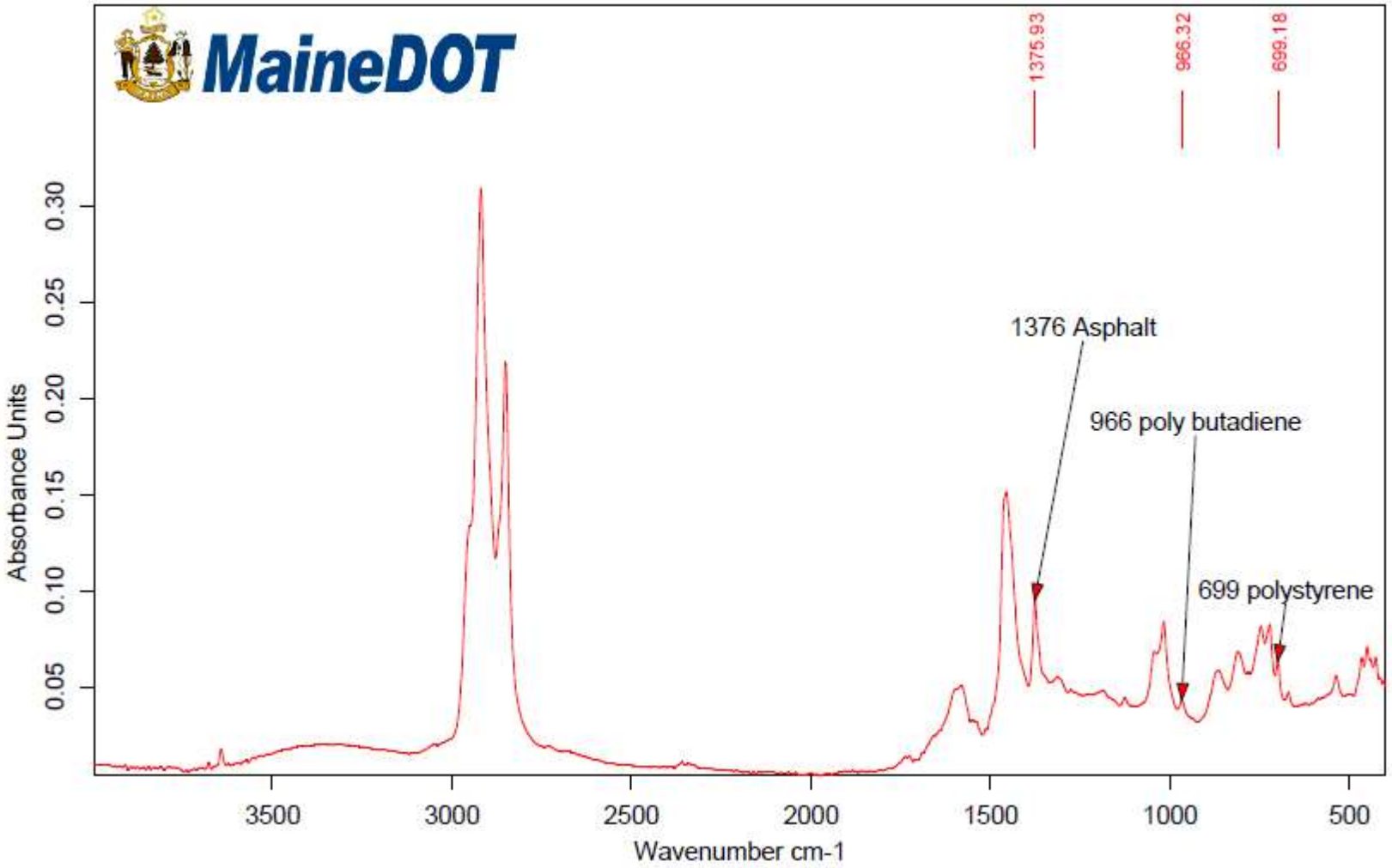
1.2. *This standard involves hazardous materials, operations, or equipment. This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. REFERENCED DOCUMENTS

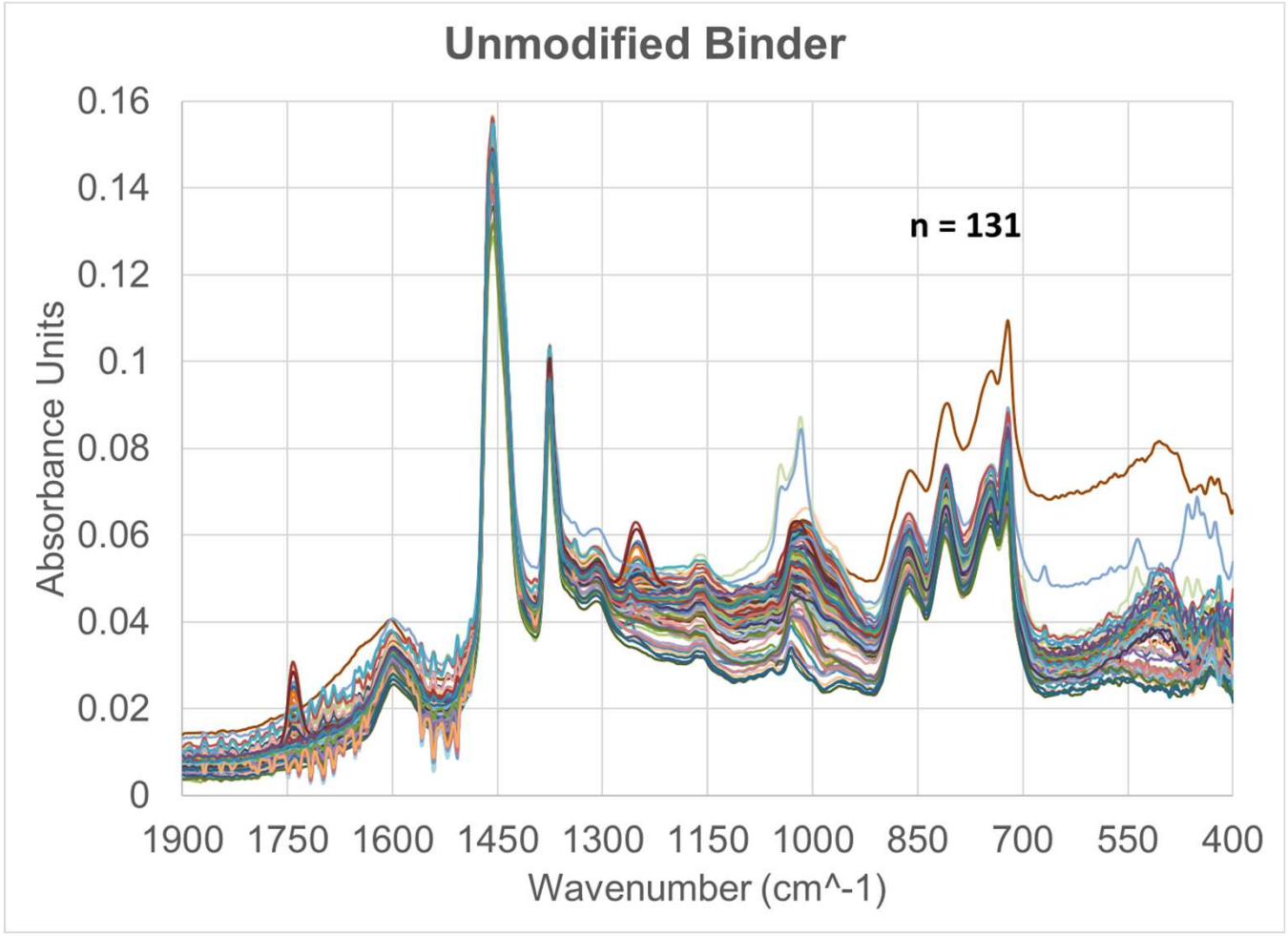
2.1. *AASHTO Standards*:

- M 231, Weighing Devices Used in the Testing of Materials

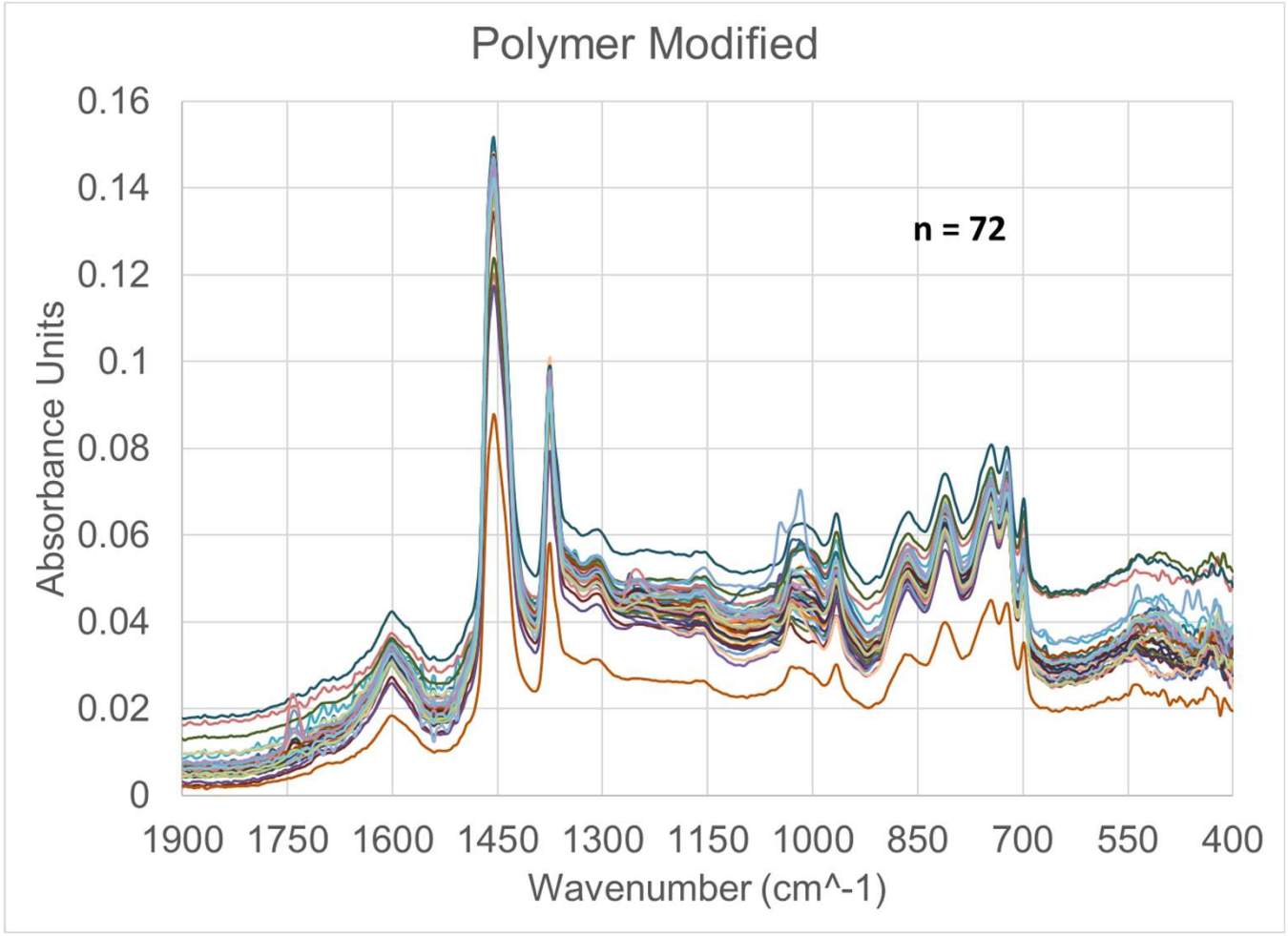
FTIR – Asphalt Binder Samples



FTIR – Standard Asphalt

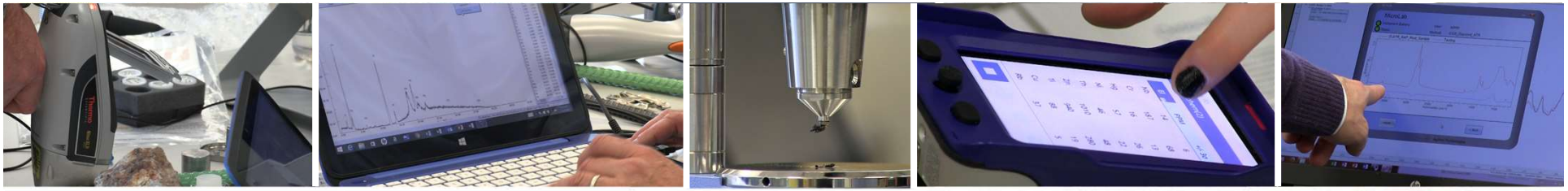


FTIR – Modified Asphalt



FTIR – Asphalt Binder

- Able to identify SBS in every asphalt binder sample labelled as being polymer-modified
- Use as a screening tool for modified grades
- Will continue to be run to create FTIR catalog of asphalt binders



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Tennessee DOT

Joe Kerstetter

U.S. Department of Transportation
Federal Highway Administration

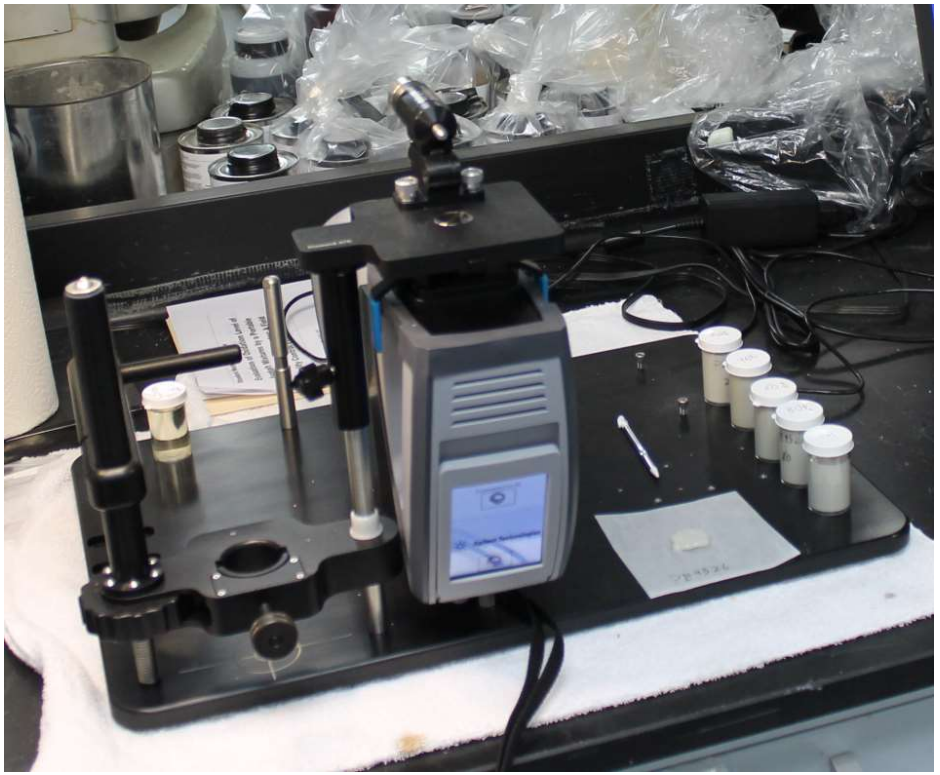
American Association of State Highway and Transportation Officials
AASHTO

R06B–Tennessee

- FTIR
  - Polymer in Binder
  - Verification of QPL products

TDOT use of FTIR

- In September of 2015, TDOT purchased two FTIR instruments for use in the Lab and Field.
- We have since created libraries for QPL products such as Texture Paint and Anti-Stripping Additives.
- We have also made a library of our Asphalt Binder Samples and have delved into research into some forensic analysis of Asphalt Cores.



Analysis of Binder in Asphalt Core

- During a recent Asphalt paving job TDOT had suspicions that a contractor may have used the wrong grade of Binder based off of contract sample testing.
- The job called for a PG 76-22, and our DSR %Recovery was about 75% too low indicating it was a PG 64-22.
- Our Field Ops personal questioned weather this PG 64-22 made it into the roadway.

Analysis of Binder in Asphalt Core

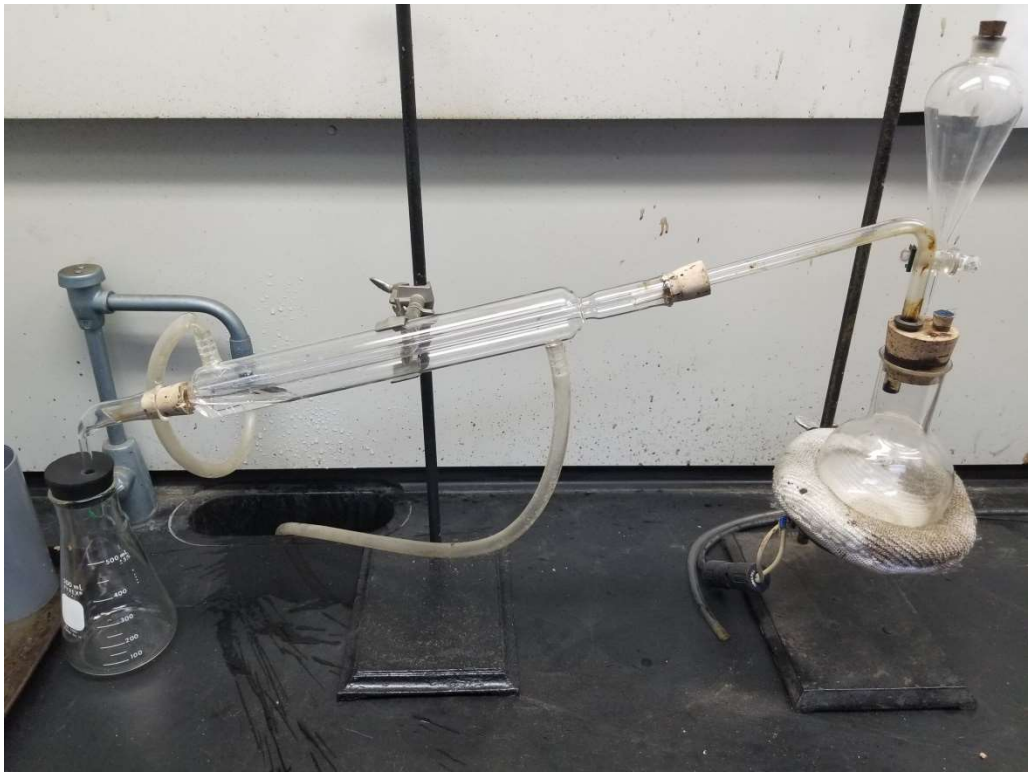
- Field Ops went out and took some cores of the asphalt in question.
- Our Asphalt Lab sawed off the layer of asphalt that needed to be verified.

Analysis of Binder in Asphalt Core

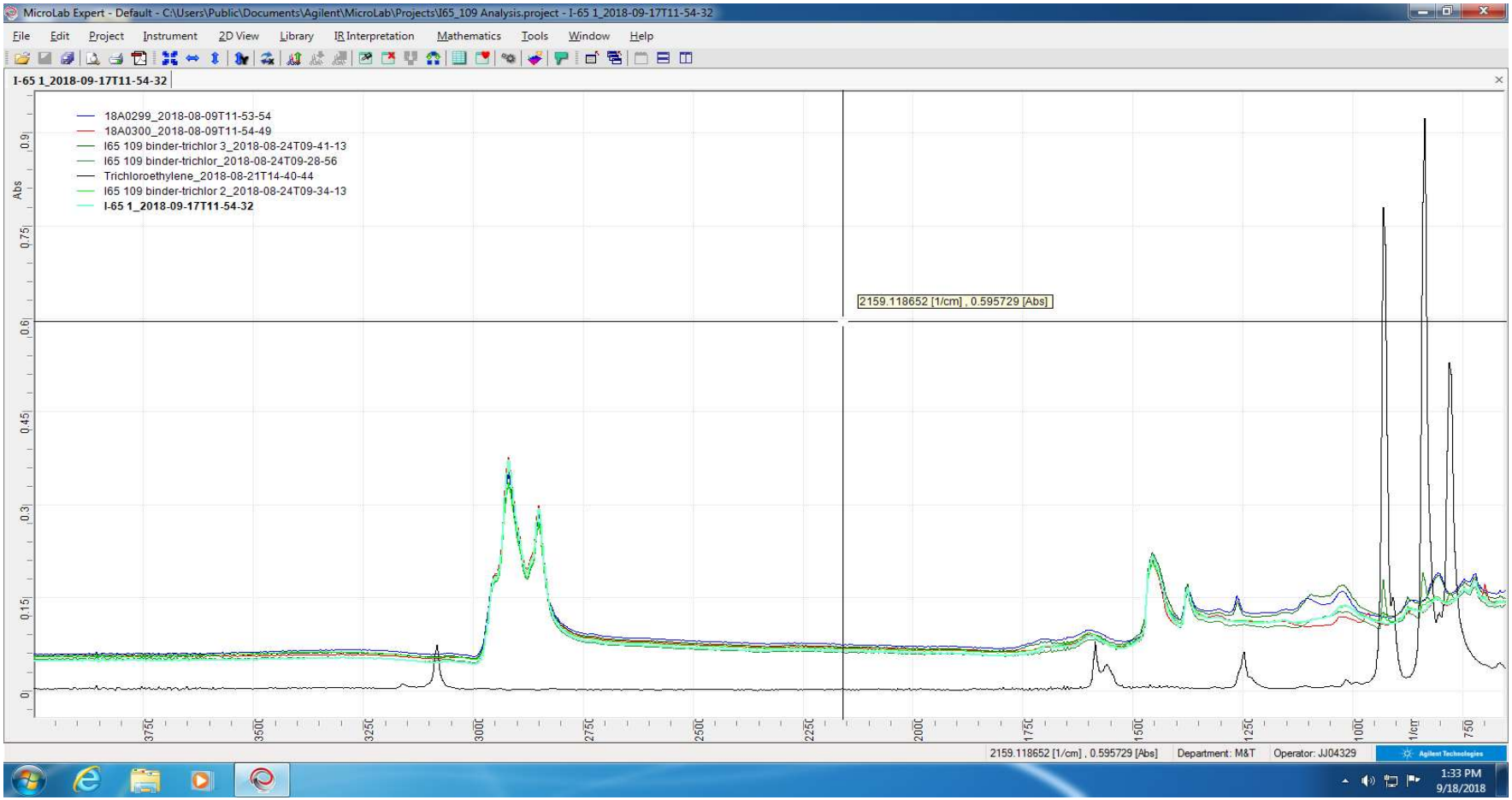
- We then did an asphalt solvent extraction on the mix from the road.
- Next we spun the resultant solvent and binder to force the dust to bottom as if we were about to run an Abson Recovery test.

Analysis of Binder in Asphalt Core

- Here instead of completing the Abson Recovery by introducing CO^2, we instead evaporated off most of the Trichloroethylene in a distillation setup.

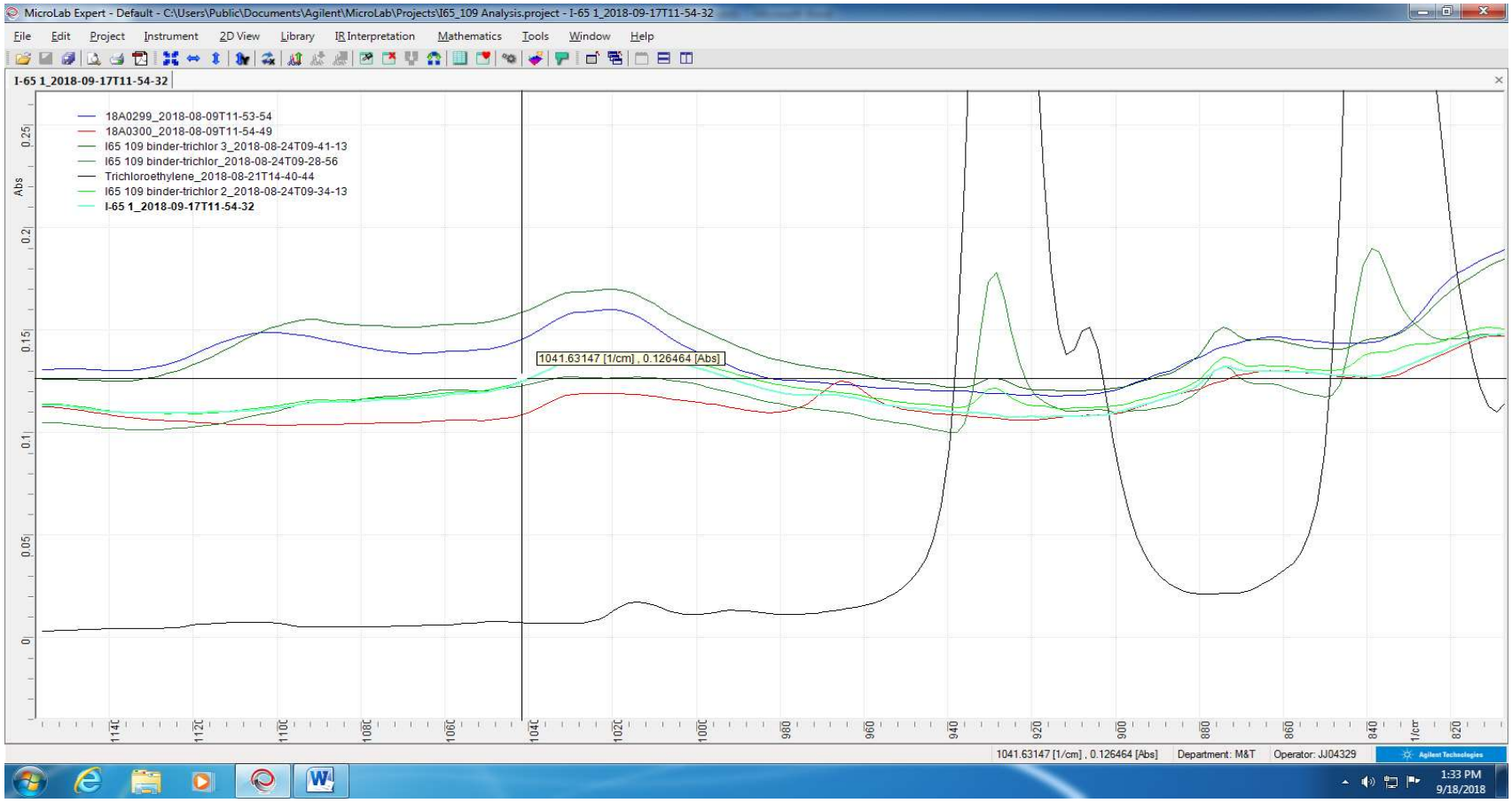


Analysis of Binder in Asphalt Core



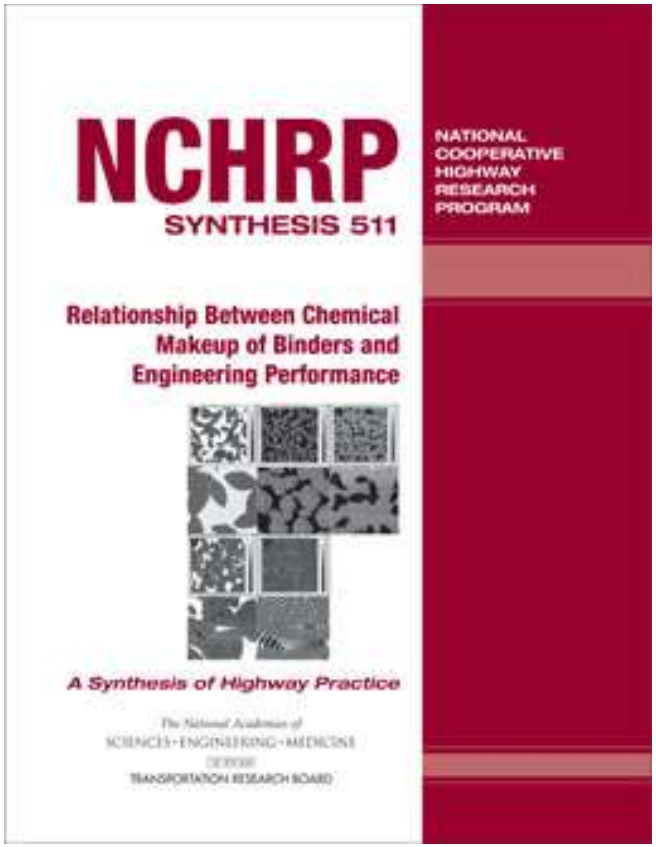
- The resulting spectra showed that the Trichloroethylene does not obscure the Polymer peak.

Analysis of Binder in Asphalt Core



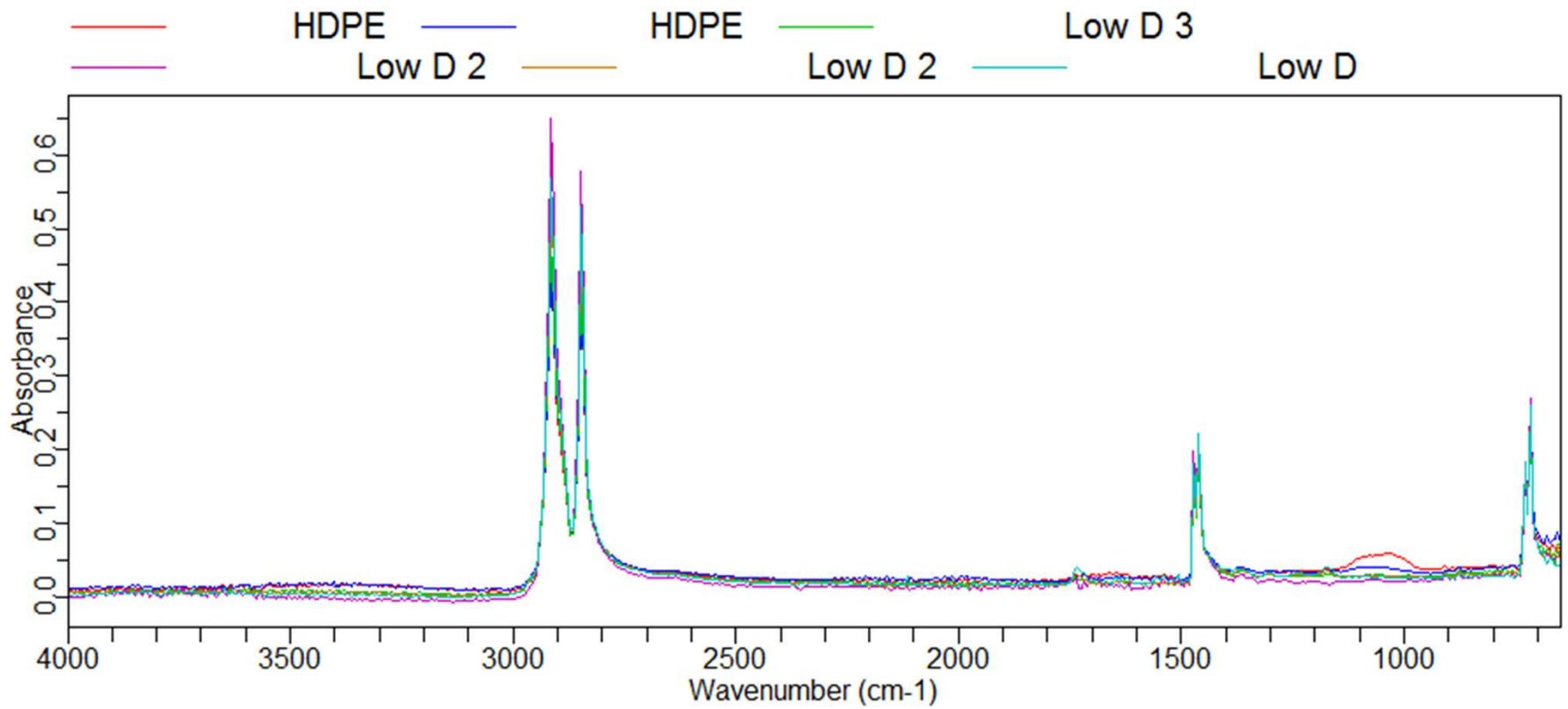
- The resulting spectra showed that none of our samples had any polymer content at all.

Analysis of Binder in Asphalt Core



- A good resource for a DOT just getting started with FTIR and XRF in Binders is NCHRP Synthesis 511

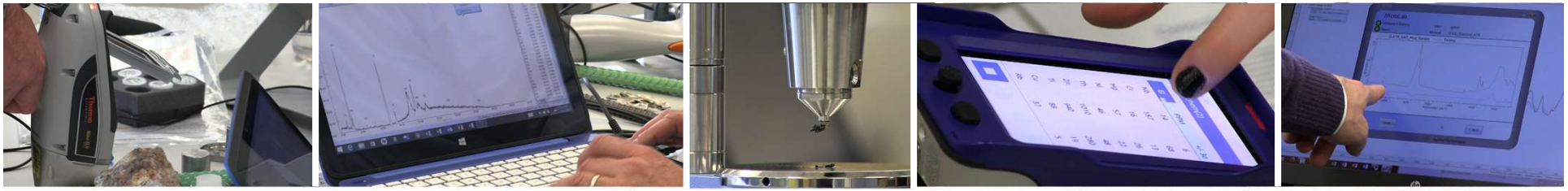
NTPEP Traffic Drum Material



- Graph shows two different manufacturers of HDPE and one LDPE drums.

Future for this Product in TN

- Looking into other materials
  - We are interested in looking at Binders using FTIR and will expand to include RTFO and PAV samples to look into aging affects of Binder and Polymer.



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Florida DOT

Cassady Allen

U.S. Department of Transportation
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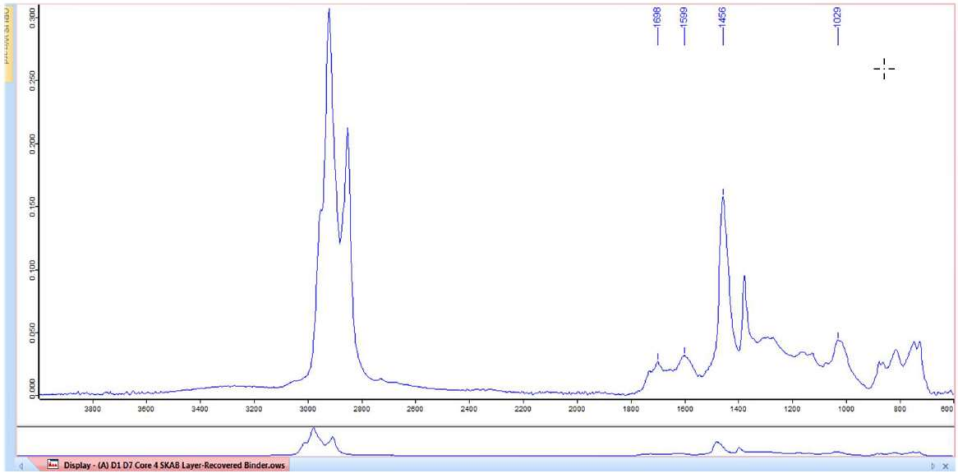
AASHTO

SHRP2 R06B: Techniques to Fingerprint Construction Materials Webinar

FDOT's Latest Uses of FTIR

Cassady Allen
March 27, 2019



Purpose of Presentation

- **This presentation will cover the following topics:**
  - Background of Field Issues
  - Previous FTIR Technology
  - Wish List
  - Portable FTIR Unit
  - Current FDOT Research
  - Next Steps

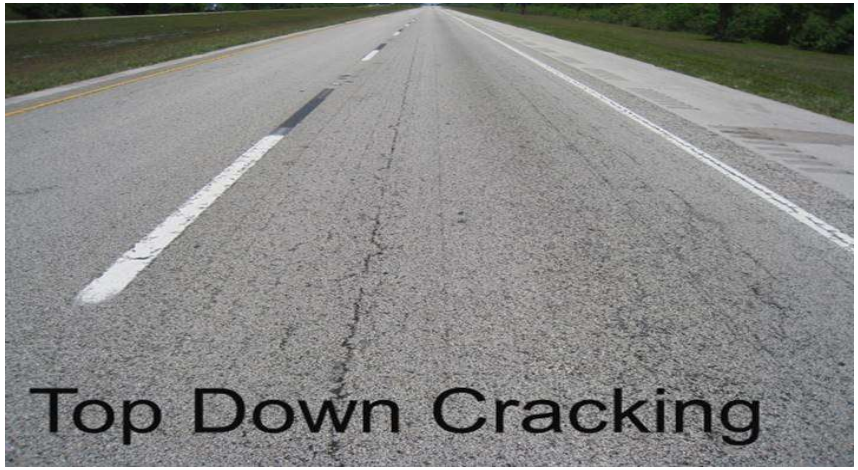
We All Have Perfect Roads…Right?

- Goal is Long Lasting Pavement
- Resources Used Wisely
- Funding Utilized Appropriately
- Customers Happy
- Easy Right?

We All Have Perfect Roads…Right?

- **Wrong**
- **Premature Roadway Failures**
  - Rutting
  - Cracking
  - Raveling
  - Etc.
- **Maintenance Related**
- **Contamination Concerns**
- **“Bonus” Items**

Field Issues



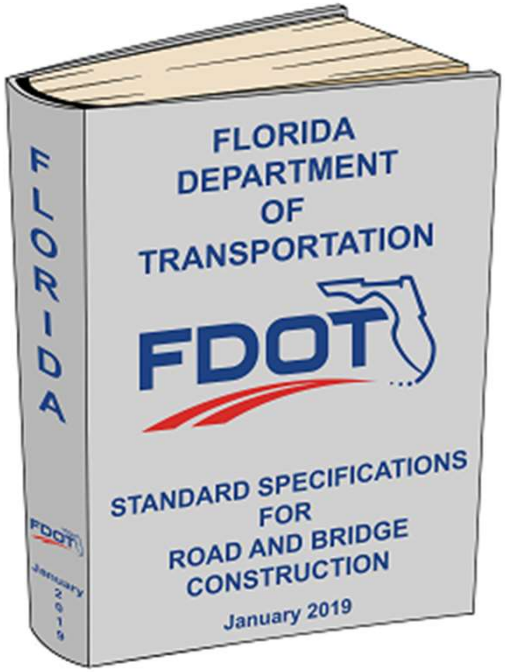
Field Issues

Field Forensics

- **Binder Issues in Field**
  - Expected Binder: PG 76-22(PMA)
  - Actual Binder: Non-Modified Grade
  - Four Known Projects
  - Performance Concerns
- **Extensive Coring/Testing**
  - Department Bears Cost
- **Mix Removed and Replaced**
  - Added Costs
  - Delays/Lane Closures
  - Time Extensions
- **Unhappy Customers**

Background

- **FDOT Binder Specs**
  - Polymer Modification
  - SBS or SB Polymer
- **Is This Reality?**
- **Numerous Samples Affected**
  - Project
  - Approved Products List
  - Accelerated Pavement Testing
- **Addressing “Bonus” Materials**
  - REOBs
  - PPA
- **FTIR fingerprint would be desirable.**



Previous FTIR Technology

- FTIR In Use Previously
- Nicolet 6700 with SMART Golden Gate ATR Module

Photo Courtesy of FDOT State Materials Office Chemistry Lab

Previous FTIR Technology

- **AASHTO T 302-15 *Polymer Content of Polymer-Modified Emulsified Asphalt Residue and Asphalt Binders***
- **Solvent-Diluted Method**
  - 1 gram of Material
  - 10 mL Solvent (Trichloroethylene)
- **Once Material is Dissolved:**
  - Teflon Infrared Windows
  - Excess Material Evaporated
  - Perform Analysis According to Specification

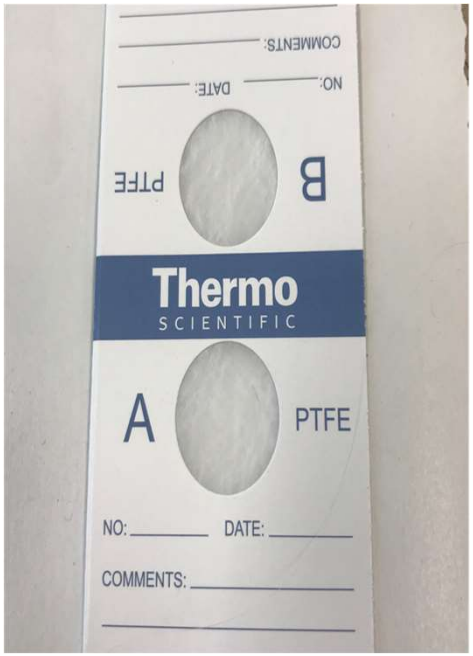
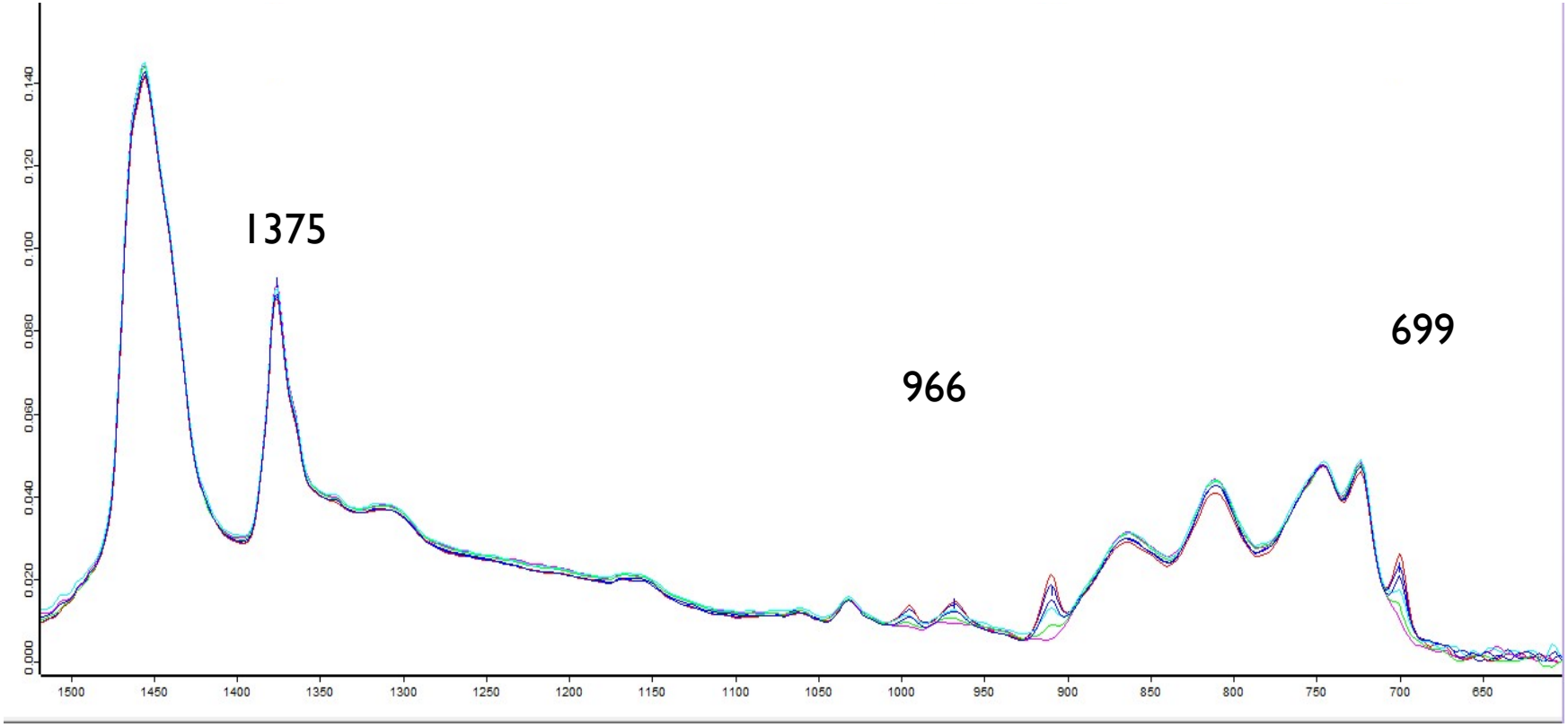


Photo Courtesy of the FDOT State Materials Office Chemistry Lab

Previous FTIR Technology



FTIR Scan Courtesy of FDOT State Materials Office

Previous FTIR Technology

- **Issues with Benchtop Units**
  - Large/Bulky
  - Not Portable
  - Expensive
  - Extensive Prep Work
  - Solvent Issues
  - Not Suitable for Field Work
- **Chemistry Lab Coordination**
- **Time Issue**
- **Better Solution Needed for Field Forensics**

Wish List - Field Applicability

- **Portable Device**
  - Place on Pavement
  - Measure %Polymer
- **Test at Asphalt Plant/Roadway**
- **Easy to Use**
- **Easy to Interpret**
  - Chemist Not Needed
- **Independent Calibration Curves**
  - Binder Source
  - SBS/SB Polymer Source

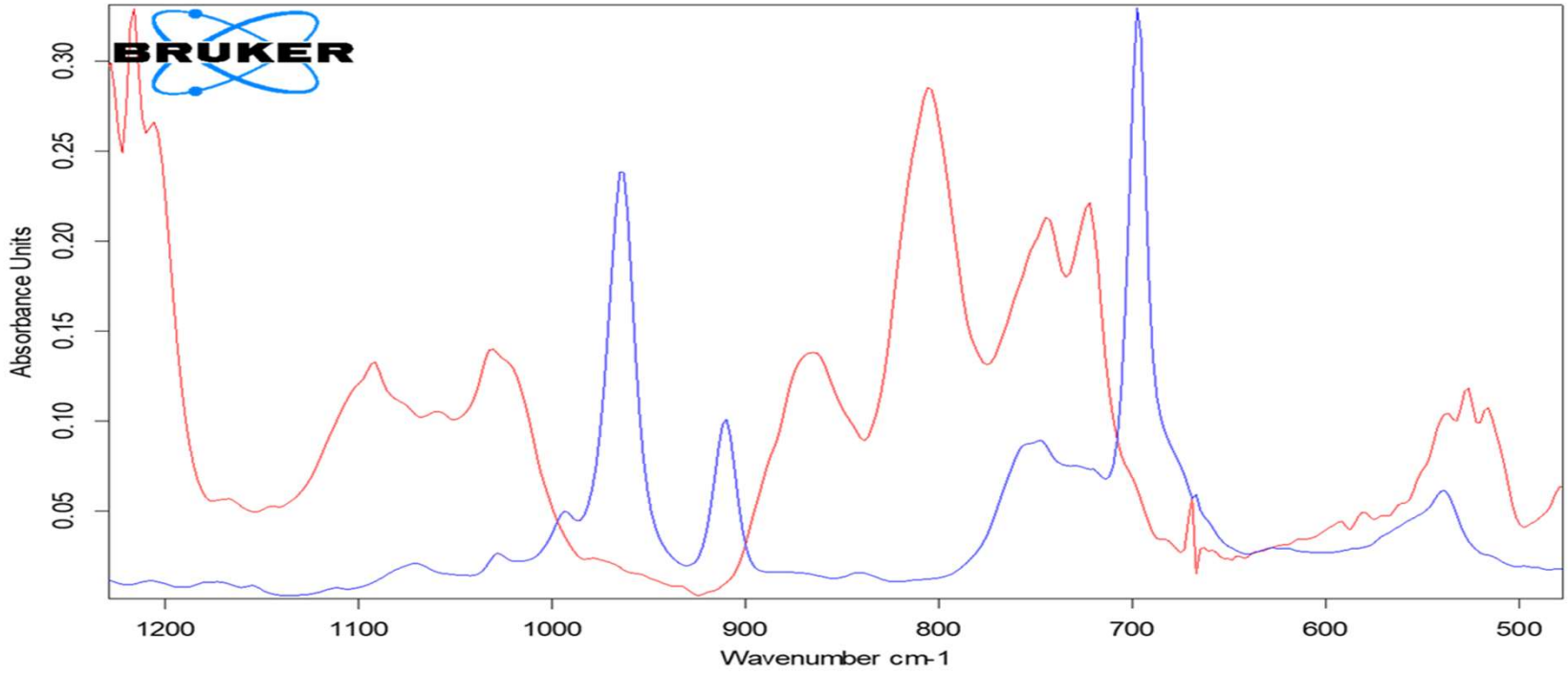
New FTIR Technology

- **Bruker Alpha with Platinum ATR Sampling Module**
  - Lightweight
  - Cost Effective
  - User Friendly
  - Small Sample
  - Acetone Solvent
- **Biggest Advantages?**
  - Portable
  - Applicable for Field Work
  - Data Obtained Quickly

Courtesy of Bruker Optics, Inc.

FTIR Technology for Asphalt

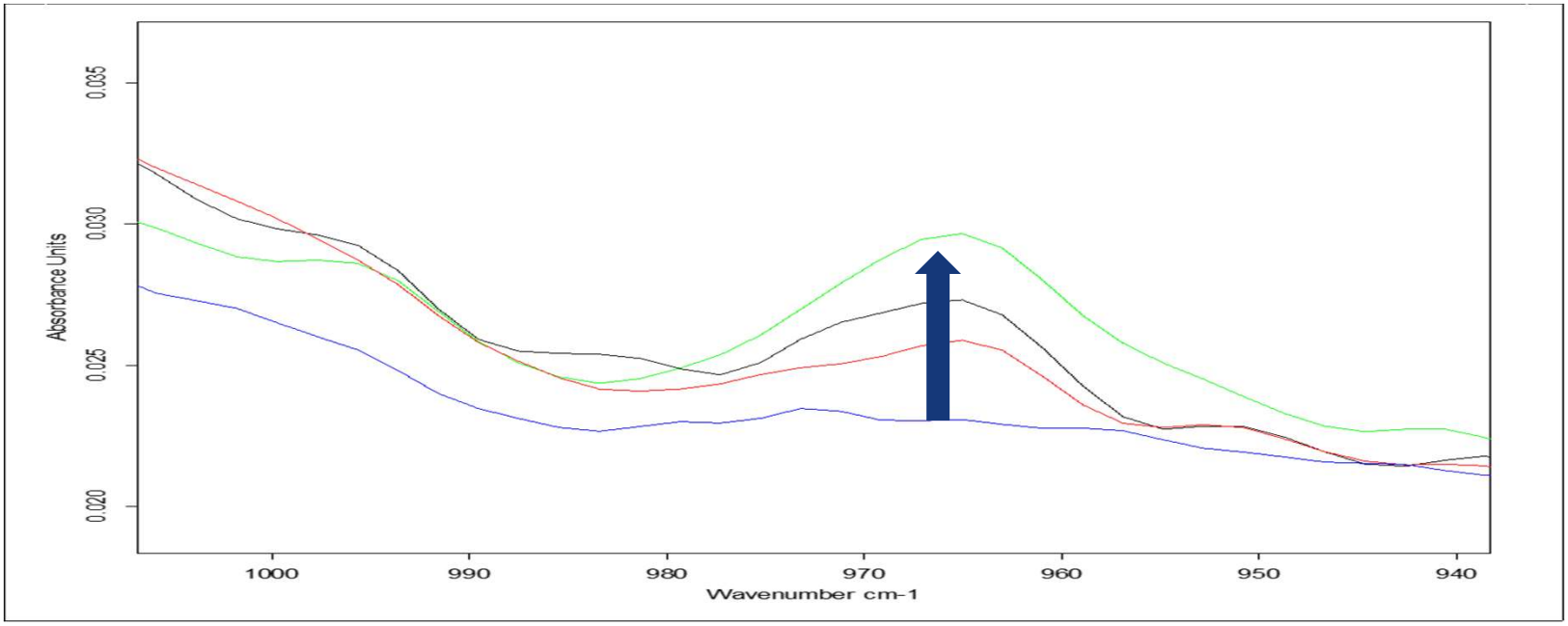
- Base Binder
- SBS Polymer



FTIR Scan Courtesy of Bruker Optics, Inc.

USF Collaboration-BDV25-977-06

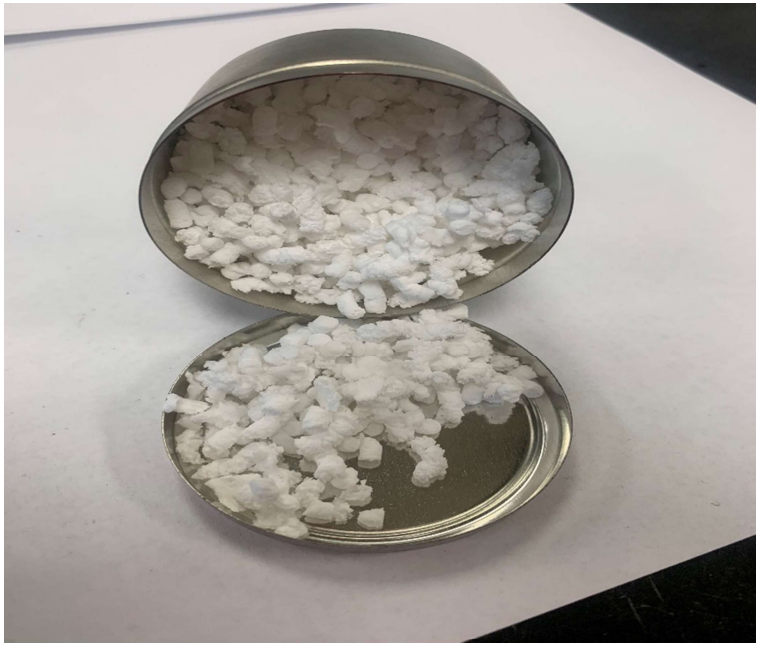
- 1375 cm^{-1} Remained Constant
- 966 cm^{-1} Peak Increased with Known Increasing SBS Concentration



FTIR Spectrum Supplied by Bruker Optics

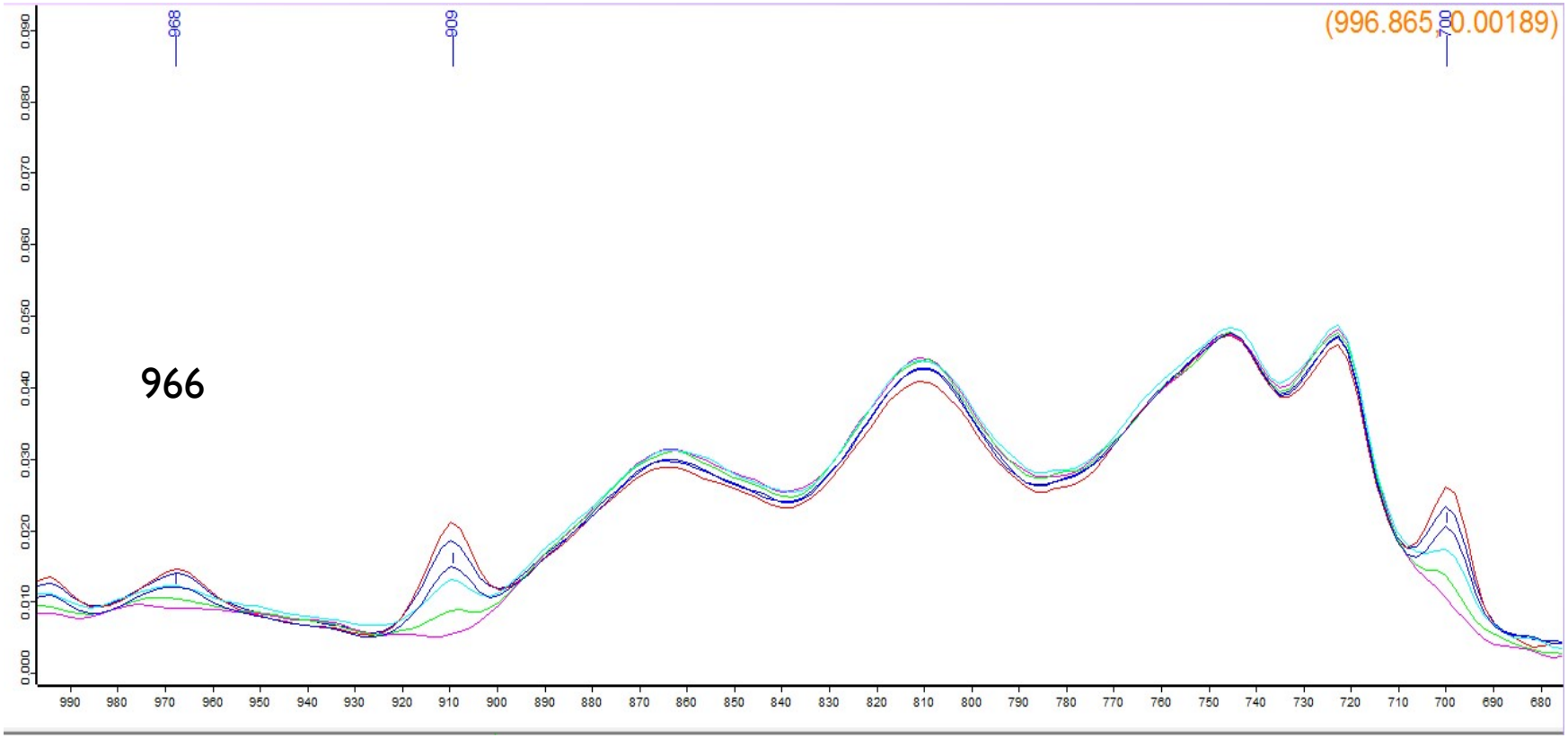
Laboratory Progress

- **Original Binder**
  - Multiple Crude Sources
  - USF Protocol
  - Modified Protocol
- **Set SBS Concentrations**
  - 0% to 10%
  - Various SBS Sources
- **Multiple Sample Measurements**
  - 1 gram Sample
- **Standard Curves Generated**



Laboratory Progress

- Similar Results to USF



FTIR Scan Courtesy of FDOT State Materials Office

Laboratory Progress

- **Benchtop Comparison**
  - Similar Spectral Results
  - Similar SBS Concentration Determinations
  - Similar Calibration Curves
- **Original Binder**
- **Recovered Binder**
  - Cores
  - Plant Sampled Materials
  - Laboratory Pills

Big Dreams in Asphalt Analysis

- **Laboratory Testing**
  - Standard Curves
  - Polymer Concentrations
  - Portable Unit Ready
- **Field Testing Applicability**
  - Field Cores
  - Laboratory Pills
  - Plant Sampled Mix

Field Applicability

- Field Cores
- Laboratory Pills
- Roadway Setting

Images Courtesy of FDOT State Materials Office and Related Personnel

Things Don’t Always Go As Planned

- Need Extracted Binder From Pavement Cores
- Time Consuming Process

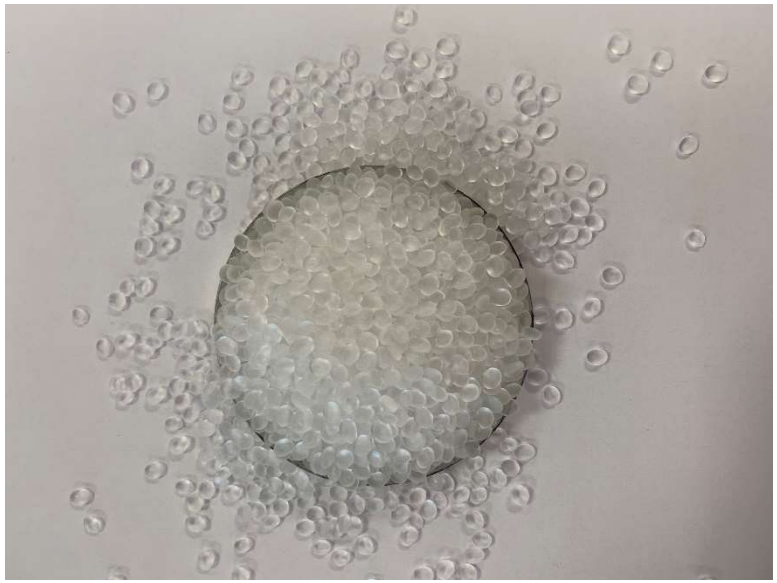
Images Courtesy of FDOT State Materials Office and Buchi Corporation

Back To The Drawing Board

- **New Techniques Needed**
  - Field Cores
  - Laboratory Pills
  - Aggregate Samples
  - Other Solid Materials
- **Ongoing Research**
  - Current Methods
  - Adjustments to Current Methods
  - Experimental Methods

Future FDOT Research

- **Calibration Curves**
  - Non Modified Binders
  - Polymer Modified Binders
  - High Polymer Binders
- **Ground Tire Rubber**
- **Anti-strip Interactions**
- **Aging Characterization**
- **“Bonus” Materials/Other Additives**
  - REOBs
  - PPA



Wish List Accomplished - Somewhat

- **Portable device**
  - Great for Liquid Samples
  - Polymer Detection
  - REOB analysis
- **Binder Analysis**
  - Asphalt Plant
  - Other Laboratories
- **Interpretation**
  - Some Guidance
  - Chemist Not Needed

Wish List Accomplished - Somewhat

- **Calibration Curves**
  - Various Binder Sources
  - Various SBS/SB Polymer Sources
- **Field Work Feasibility**
  - Aggregate Issues
  - Air Void Concerns
  - Complications
- **More Work to be Done**
  - Streamline Issues
  - Navigate Field Concerns
  - Connect Lab and Field Work

Additional FTIR Questions?

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Questions & Discussion

Questions? For More Information on R06B use these contacts.

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Additional Resources:

GoSHRP2 Website:	fhwa.dot.gov/GoSHRP2
AASHTO SHRP2 Website:	http://shrp2.transportation.org
R06B Product Page	http://shrp2.transportation.org/Pages/R06B.aspx