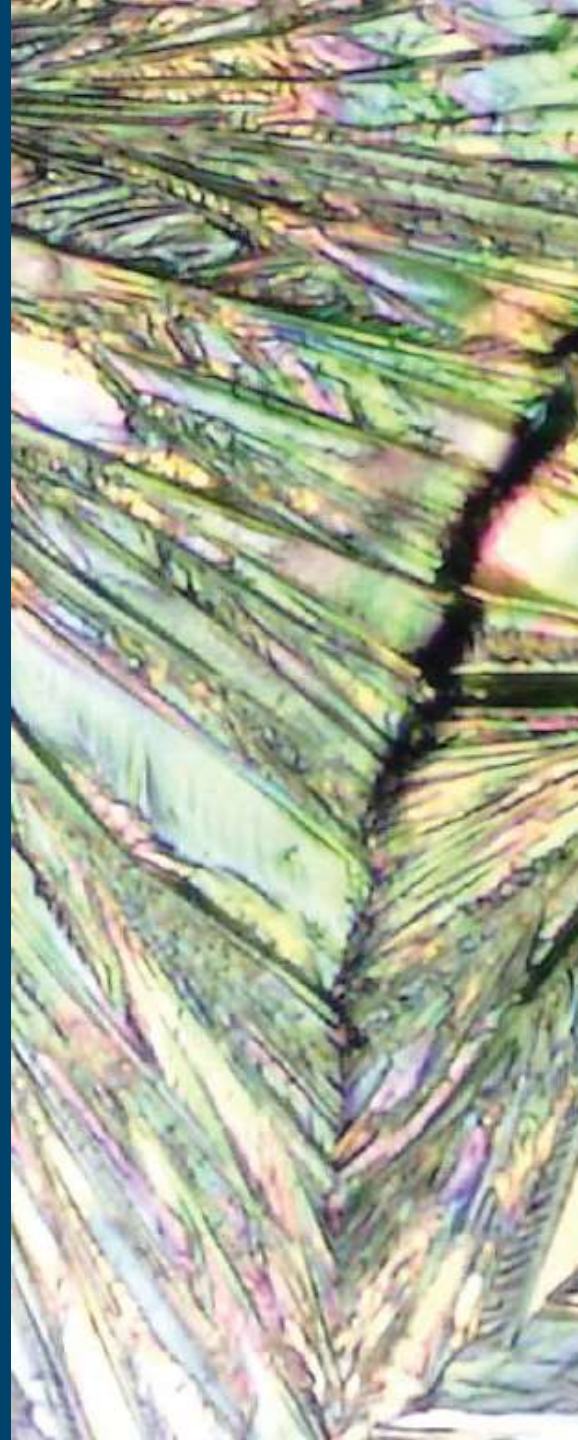


Portable and Handheld FTIR:

Bringing Real-time Identification
Capability to the Field

Keegan A. McHose
Molecular Spectroscopy
Product Specialist



Agilent At-Site FTIR Portable Analyzers



4300 Handheld FTIR

- 4.8 lbs (2.2 kg)
- Integrated computer
- “Hot swap” internal batteries
- Selectable sample interfaces
- For field use in non-hot zones



4500 Portable FTIR

- 15 lbs (6.8 kg)
- Internal battery
- USB connection to tablet or laptop
- ATR Accessory
- For field use in non-hot zones
- Cost effective

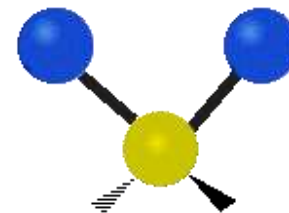
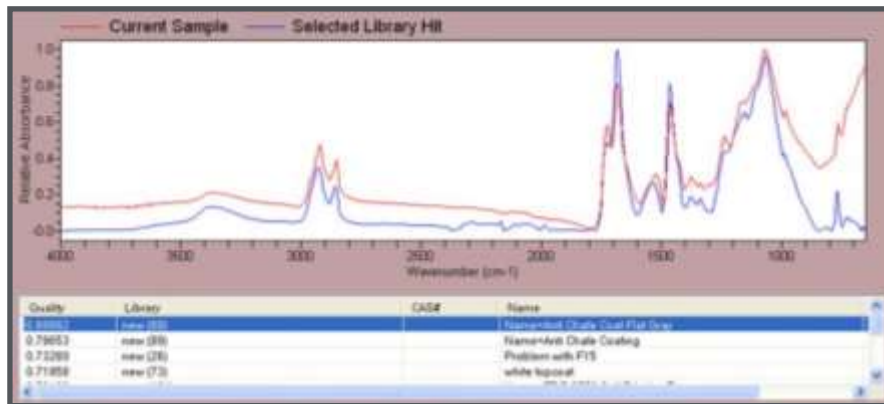


Cary 630 Portable FTIR with Microscope

- 5 mega pixel CMOS color video camera
 - 1900 μ m field of view
- Sample defining masks
 - 2000 μ m, 250 μ m, 200 μ m, 160 μ m, 100 μ m, or 60 μ m in the specimen plane
- IR sampling modes: reflection, ATR, and transmission
- Simultaneous Sample Viewing / IR Spectrum Collection

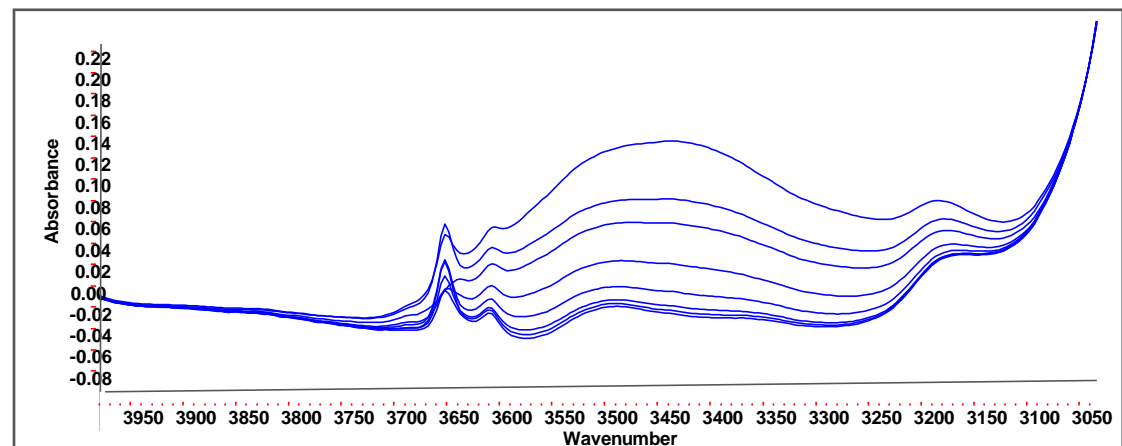
What IR Spectroscopy Provides

Each structural unit in a molecule has a unique vibrational frequency that can identify the functional group present. When all the different functional groups in a molecule are simultaneously measured, a unique molecular "fingerprint" provides the chemical identity of a sample.



↓
Quantitative analysis of sample components

↑
Spectral Identification of Unknowns

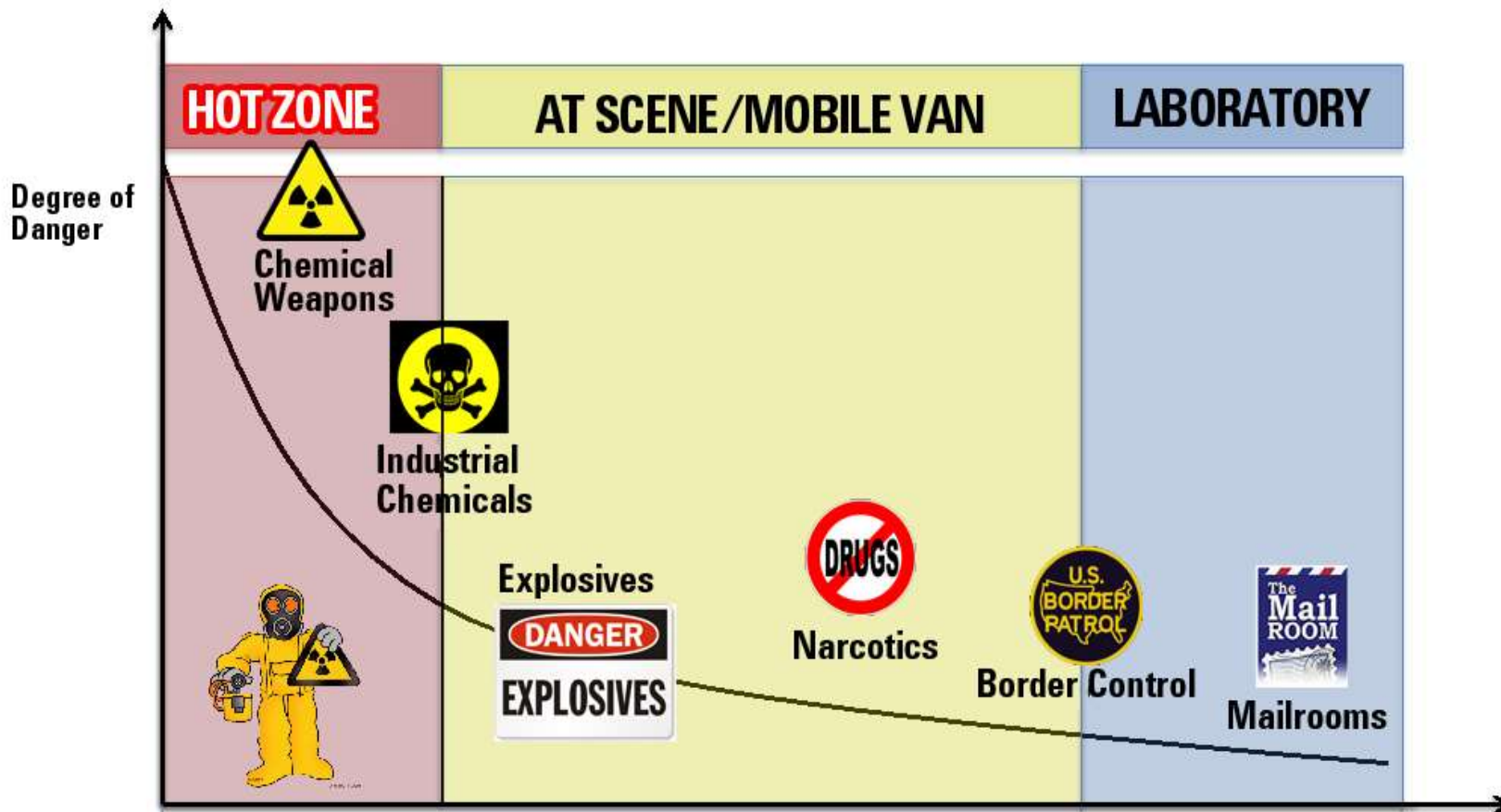


At-Site Analysis Supports Forensic Investigations

- Aid in establishing probable cause, allowing seizure of material for further analysis
- Reduce the audit trail and shorten the chain of evidence
- Enable real-time decisions about what to analyze and where to sample
- Identify the nature of a threat and establish perimeters for responders and civilians.
- Assess the progress of on-going decontamination operations and confirm remediation of the incident site.
- Aid personnel involved in border control, corporate safety, mail room and post office security
- Support the identification and seizure of counterfeit pharmaceuticals, illicit drugs and related chemicals
- Forensic analysis of toxic industrial chemicals, chemical agents, white powders, and explosives



Agilent At Site Forensic Analyzers – Cost effective and Well Suited to At-Scene and Field Lab Use



Agilent 4500/4300 FTIR

4500 Portable FTIR for At-Site Forensic Analysis



15 lbs; 8" x 11.5" x 7.5"

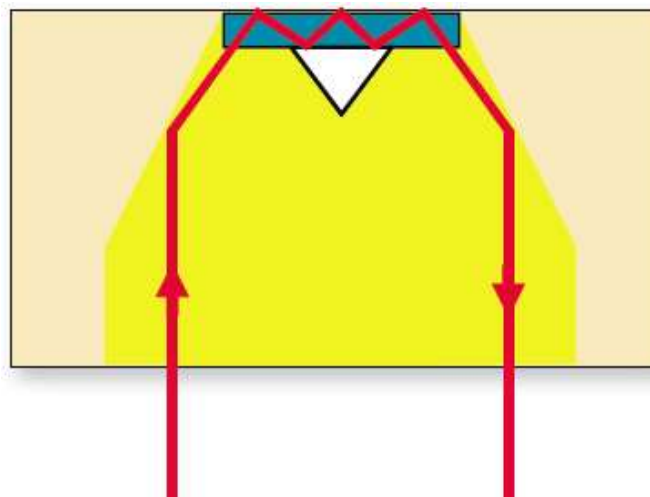
USB connection to tablet or laptop

For field use in non-hot zones

Cost effective Dedicated sample interface
(ATR shown here)

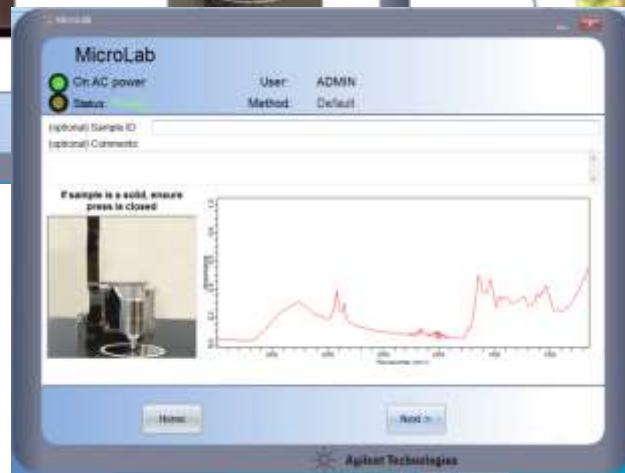
Designed for field use

3B ATR Sample Interface



- No sample preparation required, easy to use
 - <2mg sample placed on sensor,
 - pressure device ensures contact,
 - answer provided in <30 secs.
- Short path length ~2 μm
 - Library match, product identification
- Uses Diamond sensor
 - Chemical and scratch resistant
 - Internal reflection

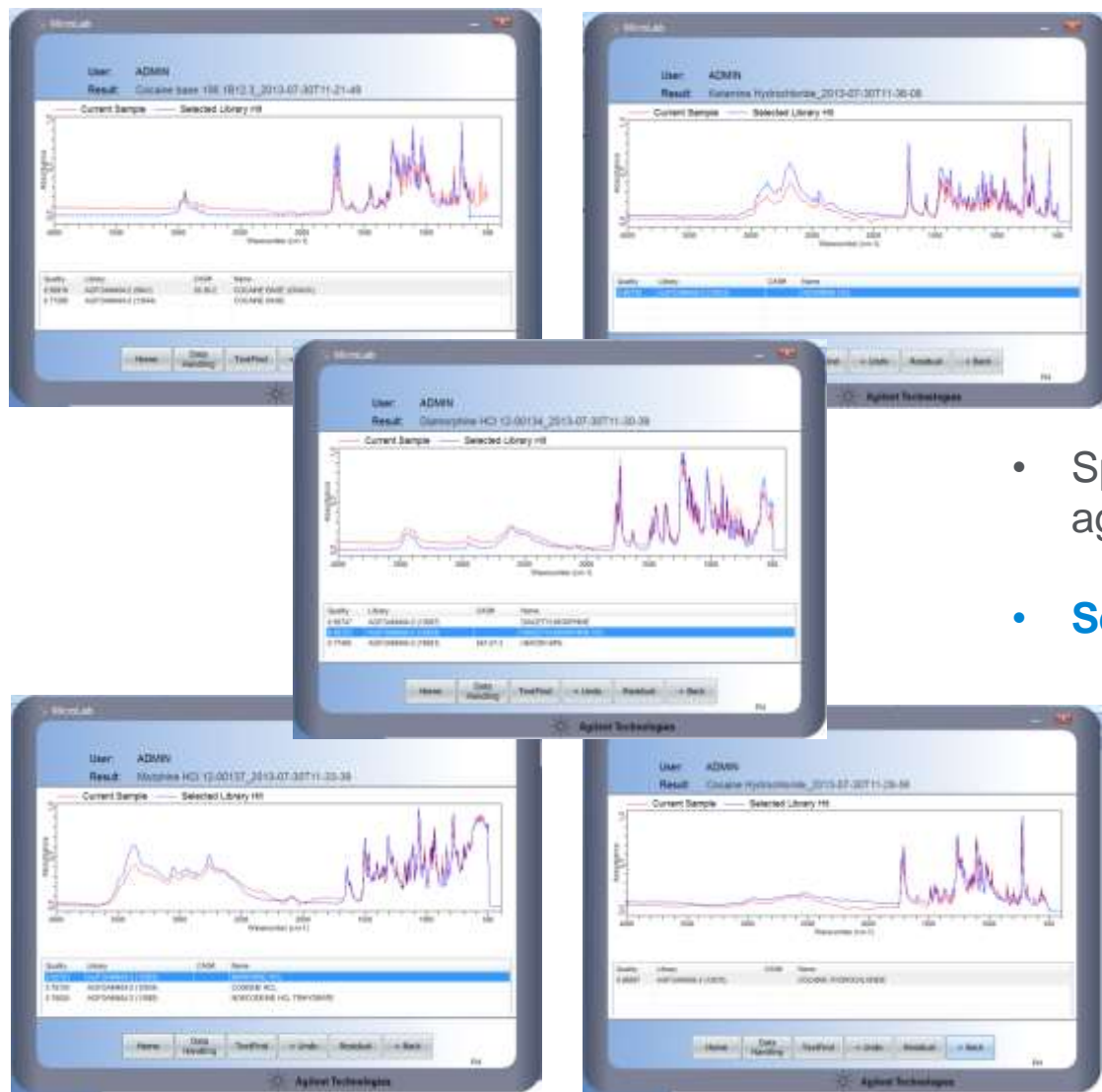
Guided User Interface



Leads analyst through the sampling process at the scene.



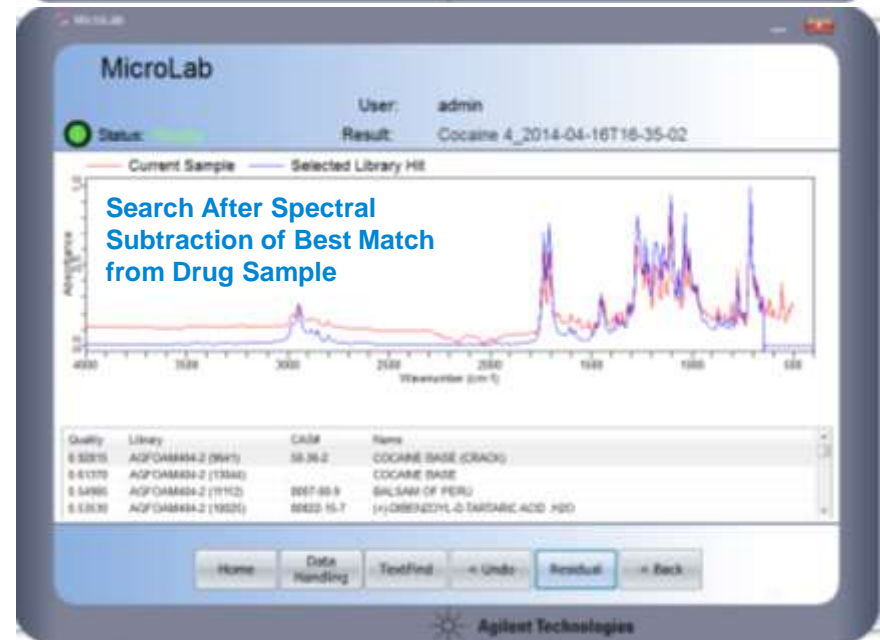
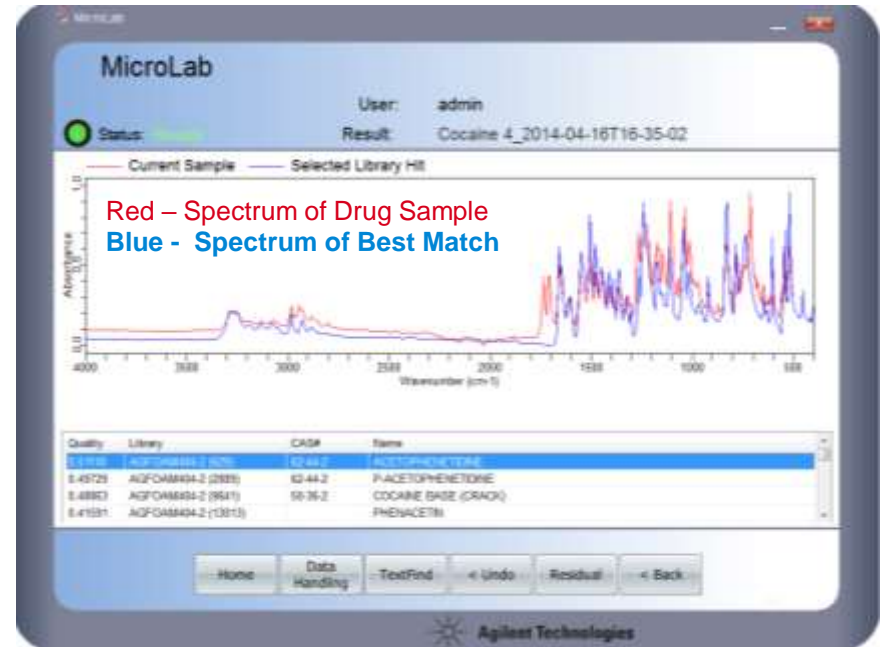
Identification of Illicit Drugs



- Spectra of street drugs searched against the Agilent Forensic Library.
- **Search reveals:**
 - ✓ spectrum of the unknown sample
 - ✓ spectrum of best match
 - ✓ sample identity
 - ✓ numerical quality of the match.

Identifying Components in Drug Mixture

- Spectral search result of a sample suspected of containing cocaine. The spectral search indicates a mixture of cocaine, acetophenetidine and p-acetophenetidine. The quality index is low due to the mixture of the two main components.
- With residual search, the first match is subtracted and the residual spectrum is automatically searched against the library.
- The residual spectrum matches well with cocaine based (crack) and the match quality is quite good.



Agilent's 4300 Handheld FTIR for At-Site Forensic Analysis

Innovative Field Readiness

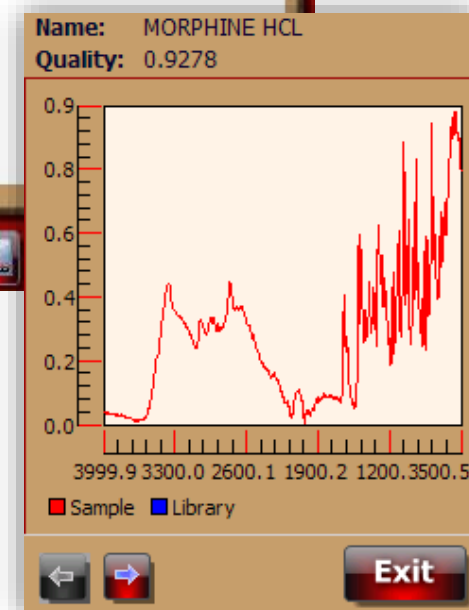
- Battery operated, “hot swappable”
- Integrated PC provides onboard data collection and analysis
- Sample interfaces to meet a wide range of complex sampling needs*
- Lightweight, balanced ergonomics
- Rugged, reliable, field proven
- 4.8 lbs (2.2 kg)



* *Diamond ATR, GE ATR, External Reflectance, Grazing Angle, Diffuse reflectance*

4300 HH FTIR Analyzer Software

- Method Driven
- Focused on Results
 - Saves original data
 - Synchronizes with PC software
- Completely functional software for Point of Measurement Applications
 - Quantitation
 - Qualitative Library Search / Identification

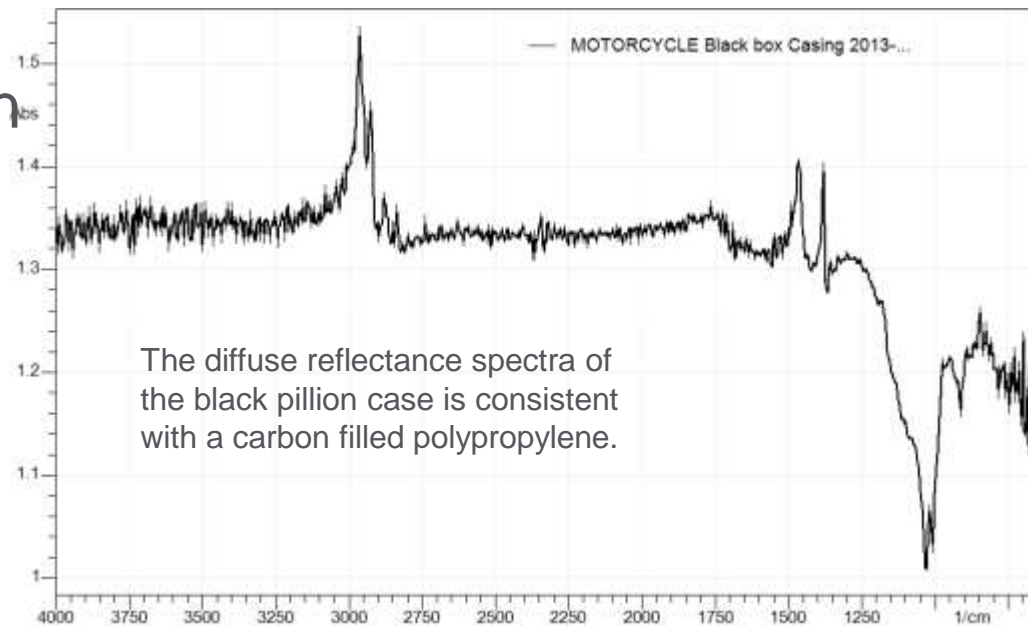


13,000 spectra from a comprehensive list of:

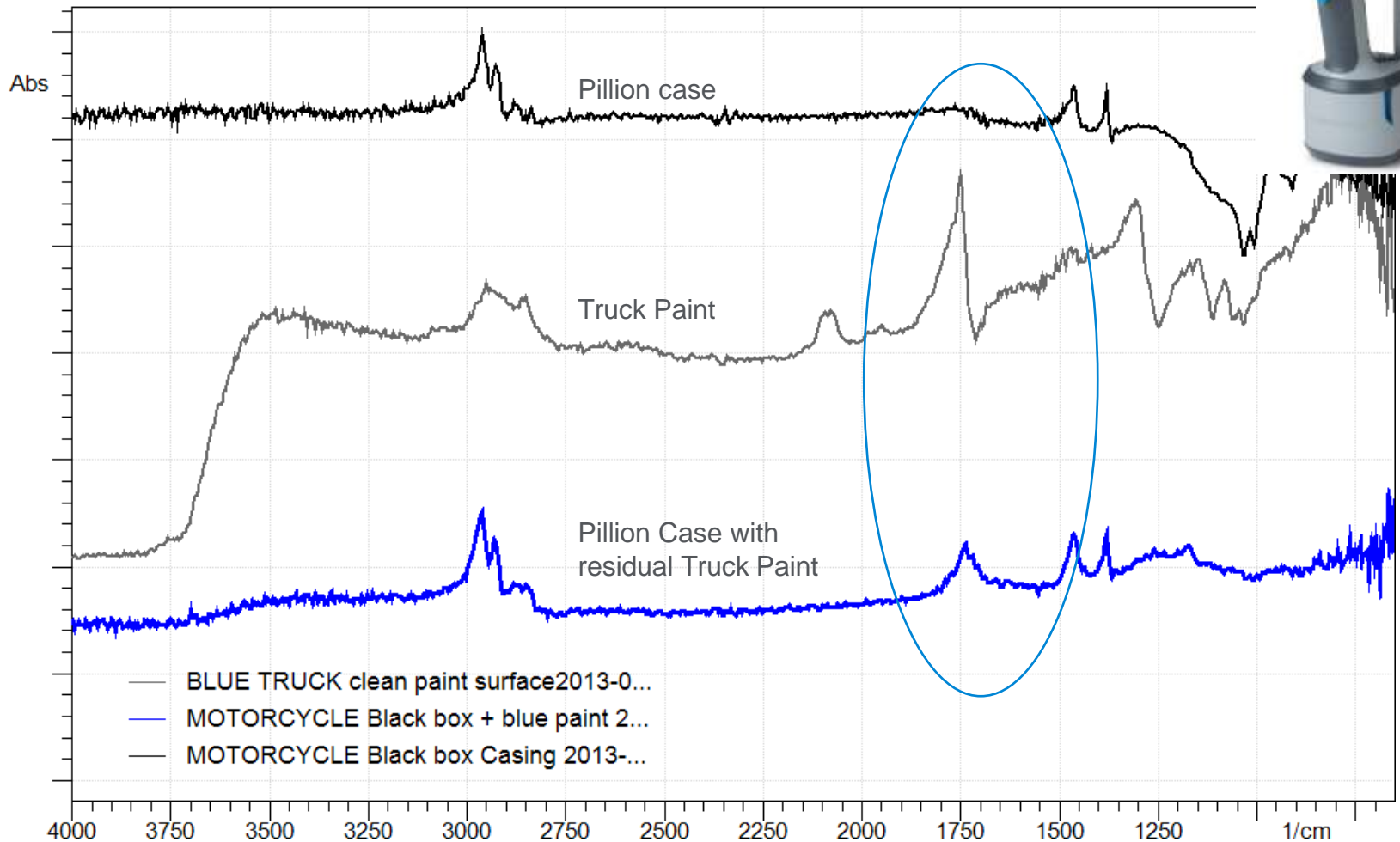
- ✓ *Bio-chemicals*
- ✓ *Forensics*
- ✓ *White powders*
- ✓ *Hazardous and Toxic Chemicals*
- ✓ *HPV chemicals*
- ✓ *Food additives*
- ✓ *Explosives*

Truck-motorcycle collision

- Handheld FTIR aided in obtaining evidence
- Investigated a blue truck that struck a motorcycle on the rear pillion case, causing a fatality
- Used diffuse reflectance FTIR of residues left on both the motorcycle and truck

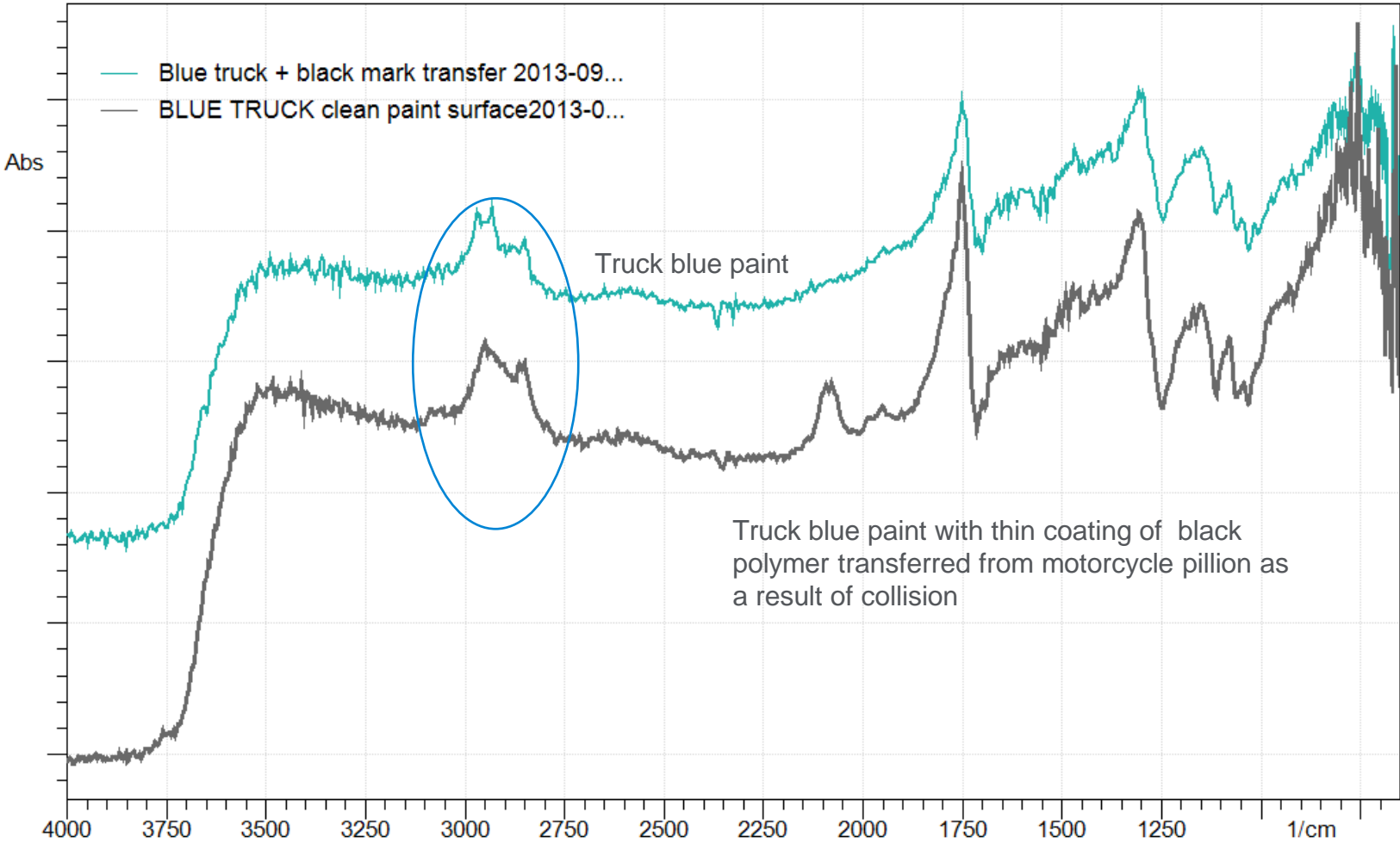


Spectra of Motorcycle and Truck Components



Truck-motorcycle collision

Black transfer mark on the blue paint of the truck

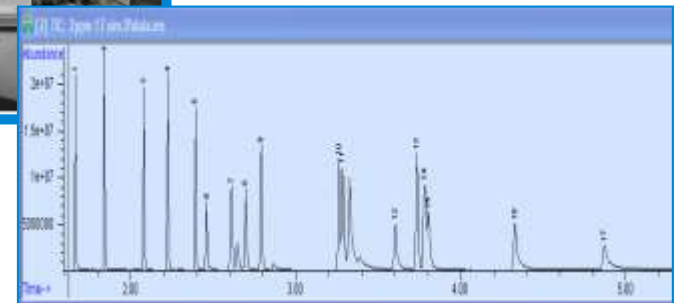
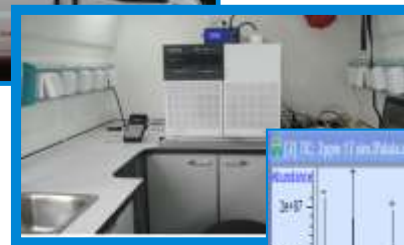
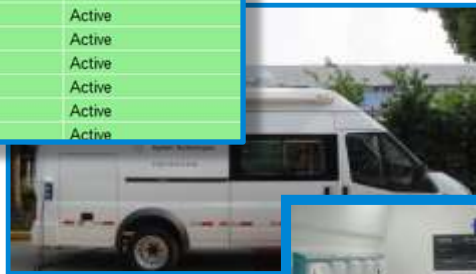


Another Real World Example – Phthalates in Toys



Status: **Ready** Result:

Part Type (i.e. Toy Doll)	
Sub Part Type (i.e. Doll's Shoe)	
Part #	
Serial #	
Lot #	
Results:	
Name	Value
Total Phthalates %	90.17 (Critical)
Plasticizer ID 1	Active
Plasticizer ID 2	Active
Plasticizer ID 3	Active
Plasticizer ID 4	Active
Plasticizer ID 5	Active
Plasticizer ID 6	Active
Plasticizer ID 7	Active



Why Phthalates?

- Phthalates have been widely used as a plasticizing agent in PVC based products; shown to be human endocrine disruptors
- Regulations have caused toy and juvenile products industries to eliminate phthalates
 - amounts greater than 0.1% are banned in children's toys and certain child care articles
 - 6 ortho-phthalates are either banned or restricted by governmental agencies (CPSC Guidelines)
- Phthalates being investigated and will be eliminated in many other industries, e.g. electronics, food, beverage and products used in the home
- RoHS directive may include phthalates in the near future (by 2016)
- Summary: a global issue crossing a number of industries



<https://www.niehs.nih.gov/health/topics/agents/endocrine/index.cfm>

Why FTIR for Phthalate Analysis?

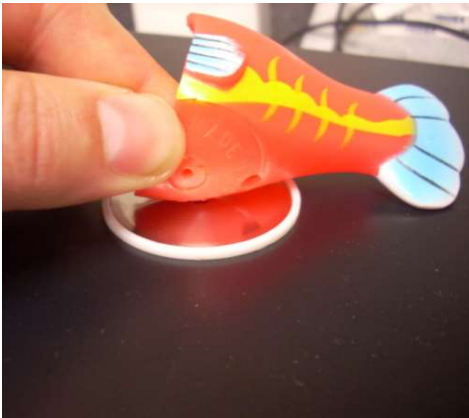
- GC-MS is the “gold standard” of analysis
 - Analytical, sensitivity, specificity
 - complicated sample prep, higher level of user expertise required, samples are measured in a lab, costly
- **Strong interest in a rapid screening method for phthalate analysis, i.e. mobile FTIR spectroscopy**
 - is fast, immediately identifies type of polymer present
 - increases analysis throughput, no sample prep required
 - provides at-location analysis as needed
 - measures total phthalates, method for PVC with LOQ to 0.1% included in Agilent Polymer Package



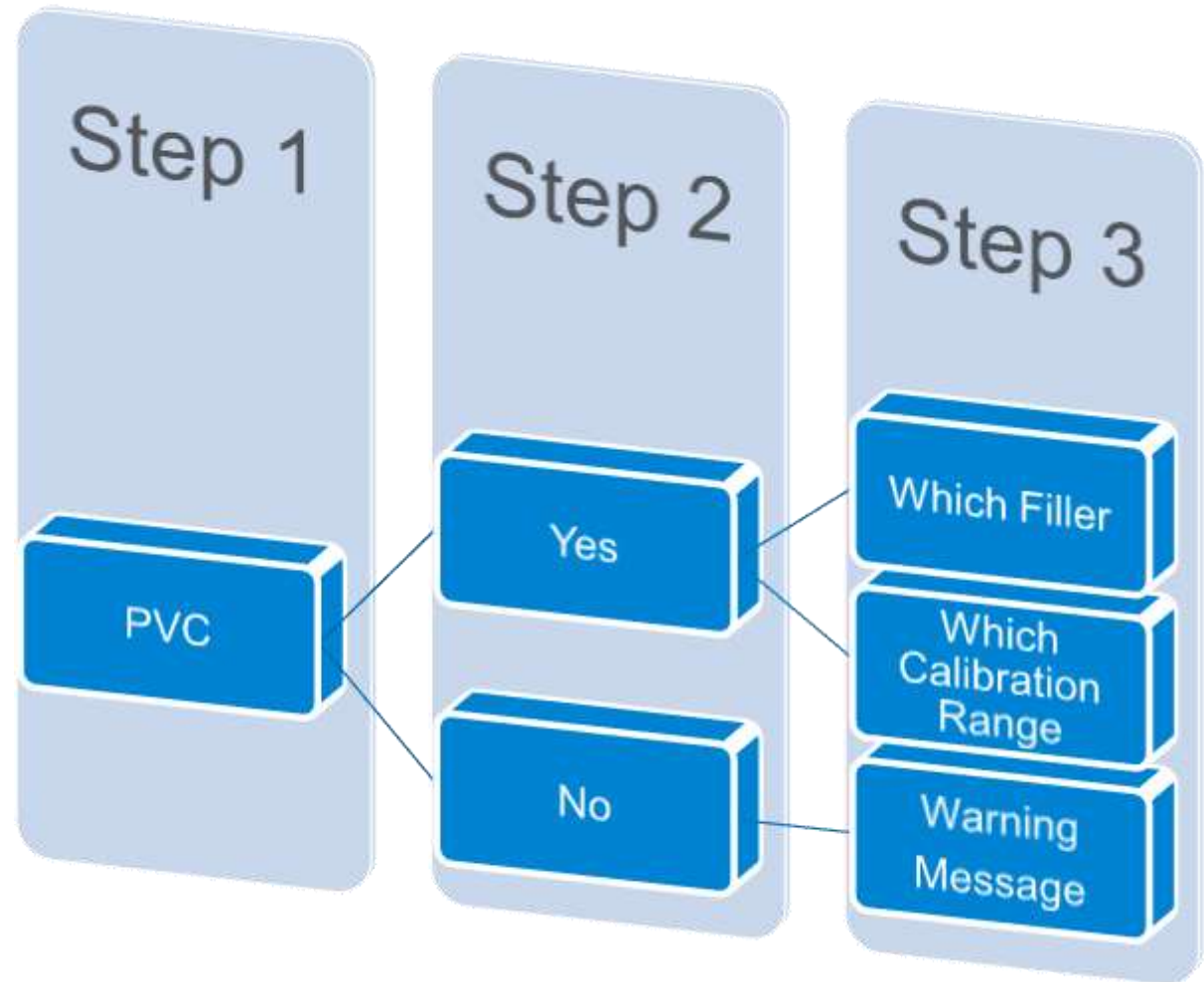
Fast screening = more samples tested
Less unnecessary work for GC-MS

Make actionable decisions in the field about samples requiring more detailed analysis
Inspect and stop restricted materials from entering marketplace

Polymer Package – 4500 FTIR Workflow

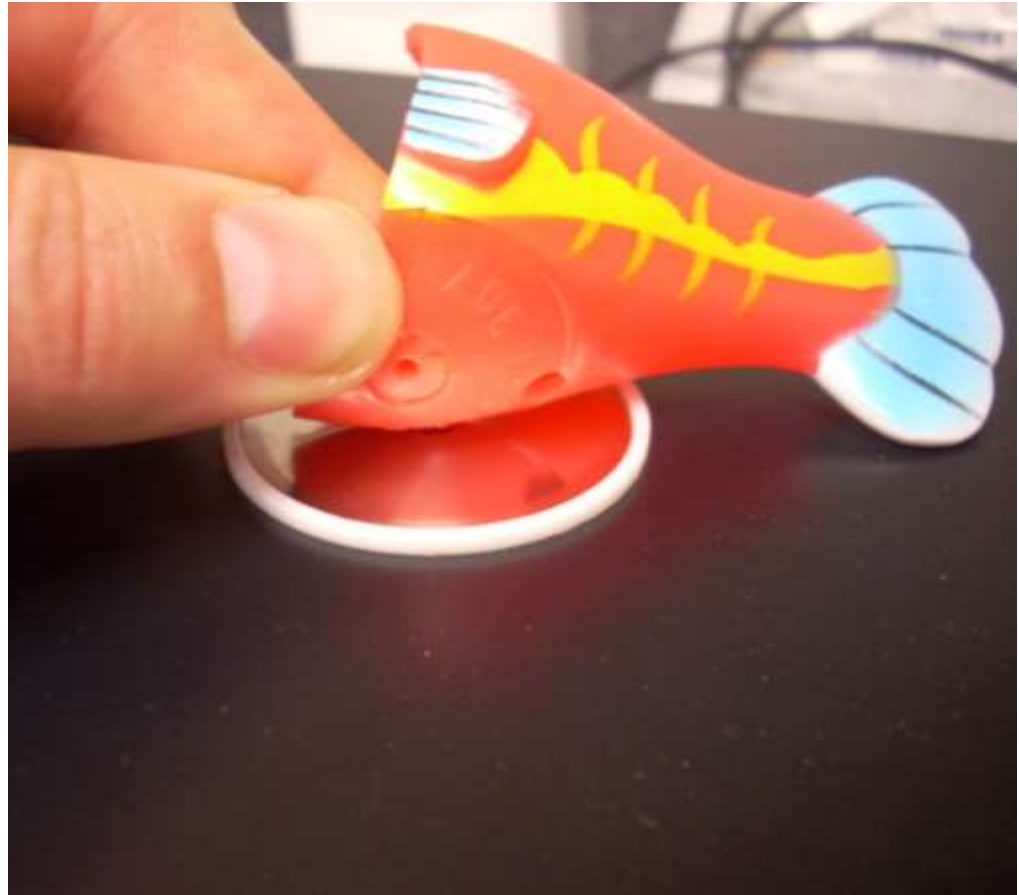


Sample is introduced to the FTIR and measured via the Polymer-Phthalates method

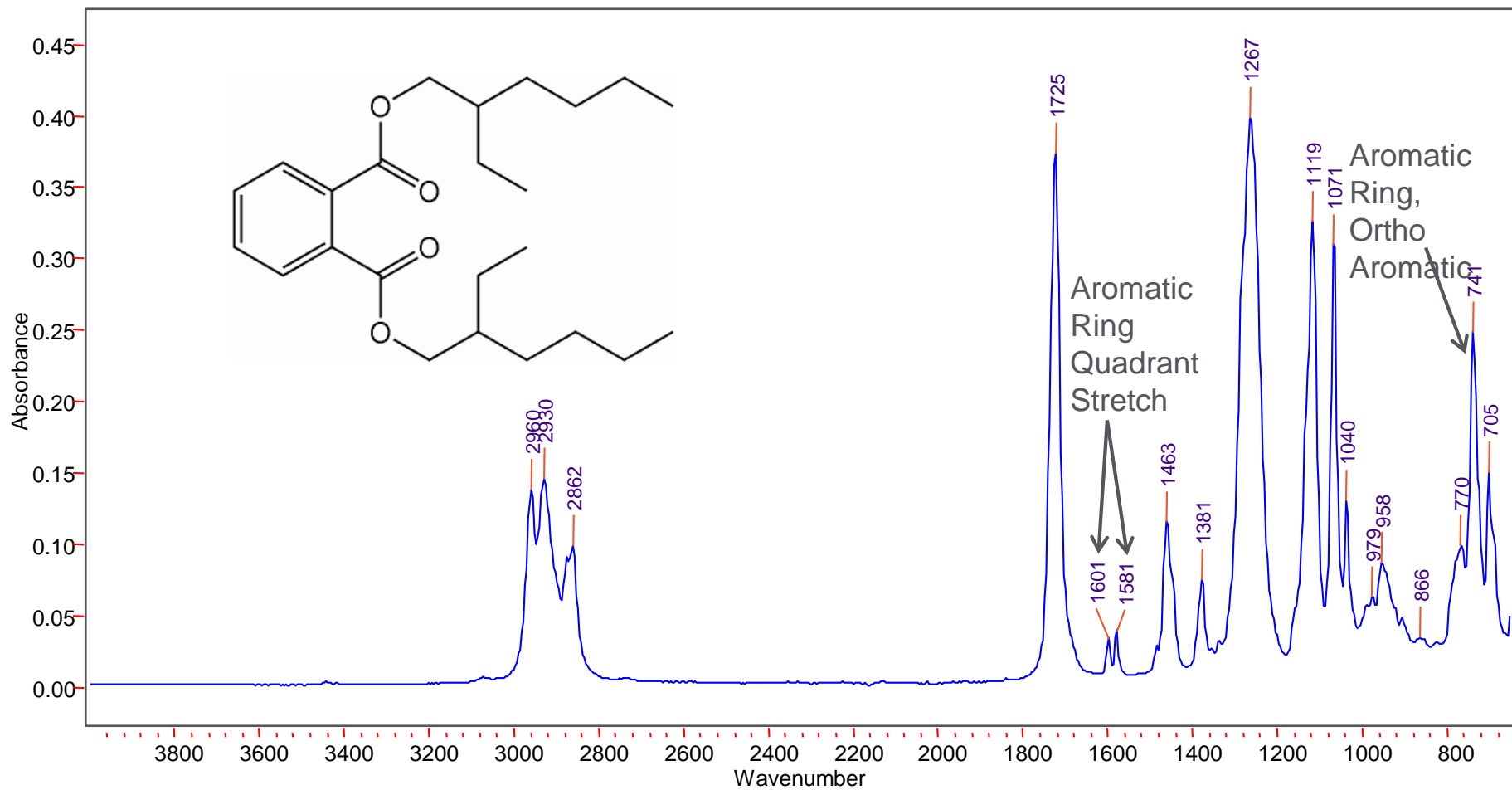


Phthalates Quantitative Analysis via Agilent 4500 mobile FTIR

- Sample is pressed flat across the diamond surface
- The slight prow of the diamond above the surface is ideal for sampling plastics
- Handles variable size samples
- No solvents required
- Non-destructive, no sample punch-out required
- Limit of Quantitation (LOQ) to 0.1% total phthalates

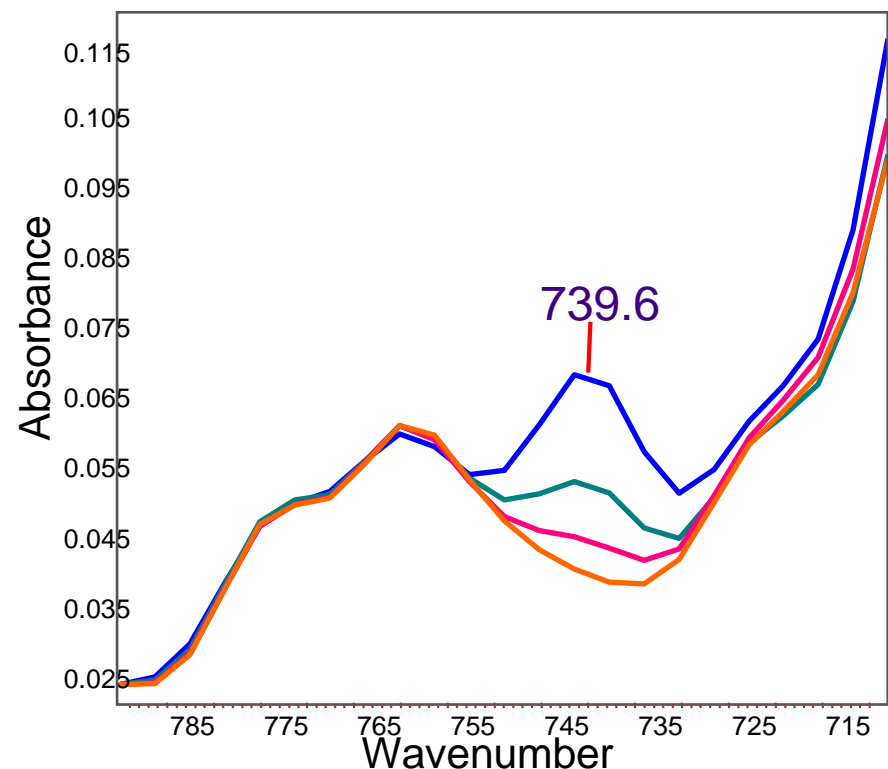
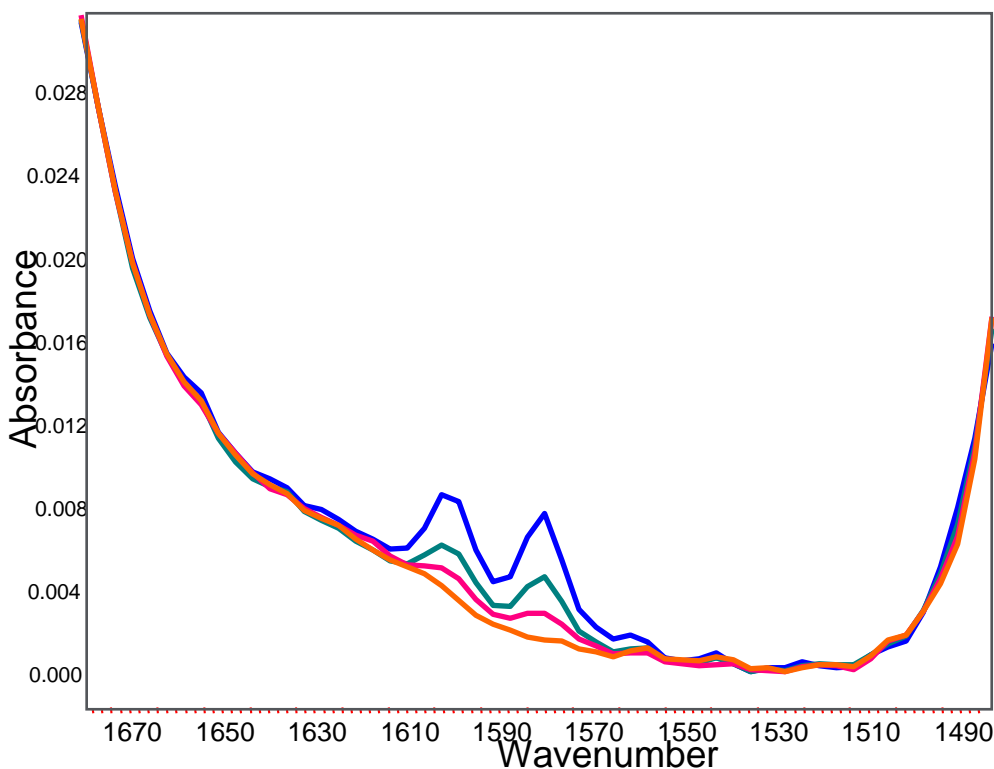


The FTIR spectrum of pure DEHP, with useful quantitative bands identified.

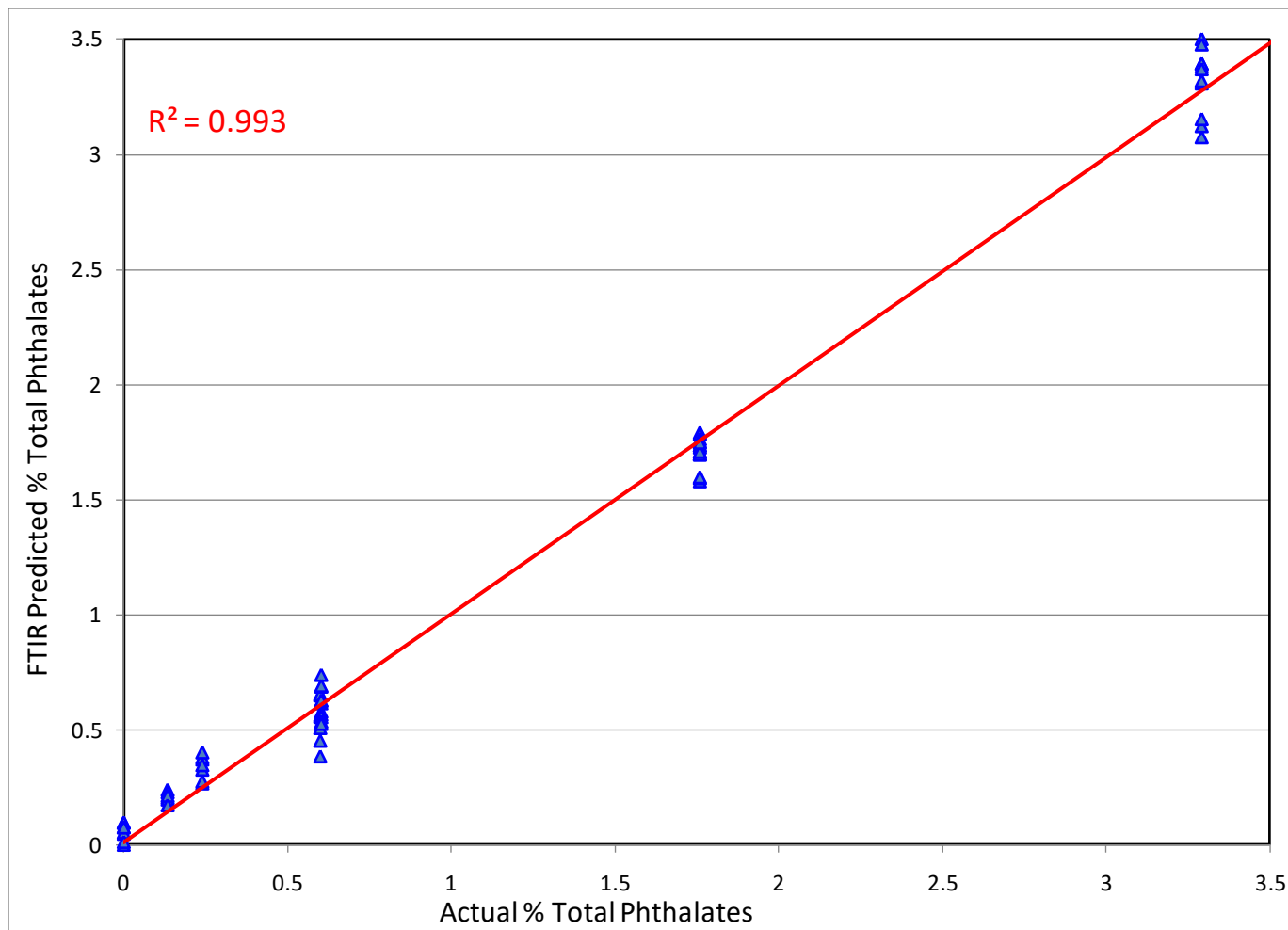


Phthalates Quantitative Analysis: 3 Bounce Diamond ATR

- PVC samples plasticized with DINCH and phthalates, 0.00% (orange), 0.60% (pink), 1.76% (green), and 3.29% total phthalates (blue).



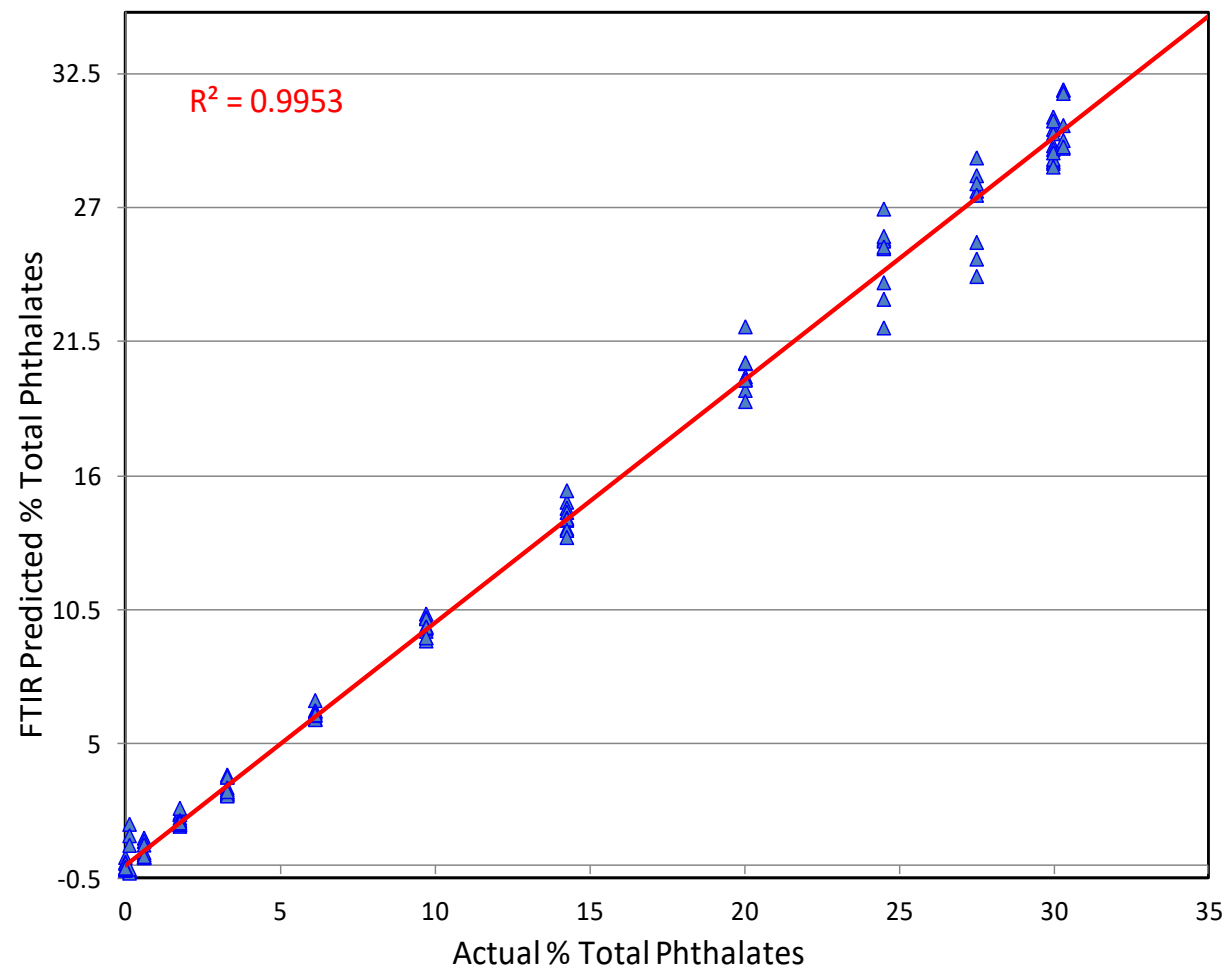
Phthalate Calibrations: Low Range (0-3% total phthalates), Multiple Instruments



Phthalate Calibrations: High Range (3-30% total phthalates) Multiple Instruments

Total Phthalates in DINCH PVC


High 3-30% Calibration	R ²	SECV
DEHP in DINCH	0.9953	0.8193
DEHP in DOTP	0.9968	0.4770
DEHP in ATBC	0.9996	0.1880
DEHP in DOA	0.9972	0.4945
DEHP in TOTM	0.9981	0.4170




Phthalates Quantitative Analysis: Example Results

The analysis results from a toy mermaid doll, made from plasticized PVC, indicate no phthalates are detected by the FTIR method.

MicroLab

 On AC power

User: admin

 Status: Ready

Result: Toy Mermaid Doll, Purple Tail_2014-11-13

Clean the ATR diamond and press ti...

Close sample press for background ...

Part Type (i.e. Toy Doll)

Sub Part Type (i.e. Doll's Shoe)

Part #

Serial #

Lot #

Manufacturer

Physical Properties (i.e. Red Soft Pla...

Date Sample Taken

Date Sample Analyzed

Location

Results:

Name	Value	Low Threshold	High Threshold
Total Phthalates %	0.00		0.5

Another look at Cocaine...

Automated Screening in seized drug samples

- Spectra of cocaine standards are shown below, (Upper) cocaine salt and (lower) cocaine base showing characteristic peak positions that were used for creating the automated method.
- To the right structural assignments to go with the selected peaks

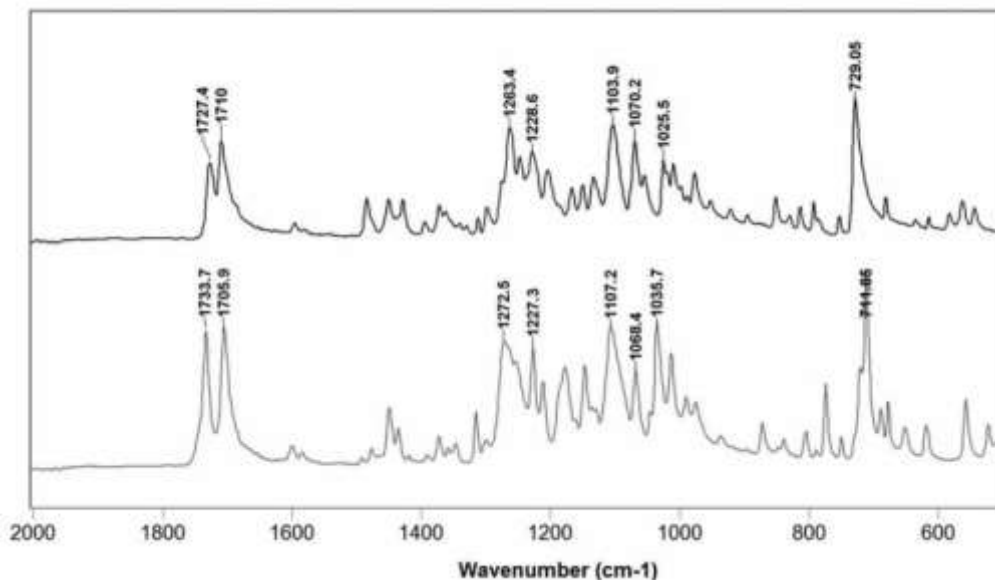
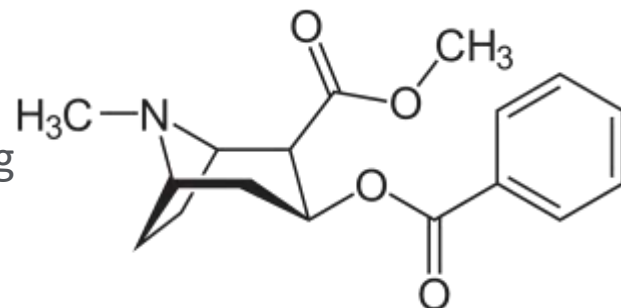


Table 1. Major ATR peak position and assignments for cocaine.

Peak no.	Vibrational mode (cm ⁻¹)		Spectral assignment ^{5,12}
	Cocaine salt	Cocaine base	
1	1728	1734	C=O stretching
2	1712	1707	C=O stretching
3	1265	1273	C-O and C-N stretching
4	1230	1227	Acetate C-O stretching
5	1105	1107	C-O and C-N stretching
6	1071	1068	Mono substituted benzene stretching
7	1026	1035	Mono substituted benzene stretching
8	729	712	C-H out of plane bending

Another look at Cocaine...

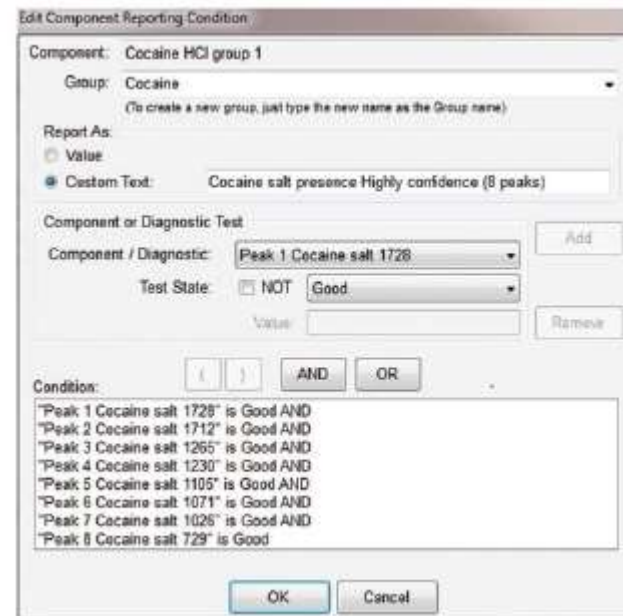
Automated Screening in seized drug samples

The table below shows how the reporting classification is derived. Based on the number of peaks identified when running the method, a report likelihood is returned.

To the right is how that conditional analysis is developed in MicroLab software.

Cocaine salt peaks (cm ⁻¹)	1728	1712	1265	1230	1105	1071	1026	729	No. of peaks identified by the method	Evidence of cocaine in seized sample
X	X	X	X	X	X	X	X	X	8 peaks	High confidence
X	X	X	X	X	X	X	X	X	7 peaks	High confidence
X	X	X		X	X	X	X	X	7 peaks	High confidence
X	X	X	X	X	X	X	X	X	7 peaks	High confidence
X		X	X	X	X	X	X	X	7 peaks	High confidence
X		X		X	X	X	X	X	6 peaks	Certain
X	X	X		X	X			X	6 peaks	Certain
X	X			X	X			X	5 peaks	Most likely
X	X	X		X				X	5 peaks	Most likely
X	X			X				X	4 peaks	Likely

Cocaine base peaks (cm ⁻¹)	1734	1707	1273	1227	1107	1068	1035	712	No. of peaks identified by the method	Evidence of cocaine in seized sample
X	X	X	X	X	X	X	X	X	8 peaks	High confidence
X	X	X		X	X	X	X	X	7 peaks	High confidence
X	X		X	X	X	X	X	X	7 peaks	High confidence
X	X			X	X	X	X	X	6 peaks	Certain
X	X			X	X			X	5 peaks	Most likely
X	X			X		X		X	5 peaks	Most likely
X	X			X				X	4 peaks	Likely



MicroLab Software's component reporting feature used to set the conditions for peak combinations to indicate the probability of the presence of cocaine. For each peak to satisfy "good" condition, the peak should be present in the spectrum.

Another look at Cocaine...

Automated Screening in mixed samples

Sample	Instrument Cary 630*	Results based on peak picking method		
		Cocaine form	No. of peaks	Cocaine presence probability (via FT-IR)
1	Cocaine (17%) + related compounds, phenacetin and tetramisole	Base	5	Most likely
2	Cocaine (27%) + related compounds, phenacetin and tetramisole	Base	6	Certain
3	Cocaine (26%) + related compounds, phenacetin and tetramisole	Salt	6	Certain
4	Cocaine (38%) + related compounds and phenacetin	Base	7	High confidence
5	Cocaine (6%) + related compounds and phenacetin	Base	4	Likely
6	Cocaine (34%) + related compounds and phenacetin	Base	6	Certain
7	Cocaine (17%) + related compounds, phenacetin and tetramisole	Base	5	Most likely
8	Cocaine (26%) + related compounds, phenacetin and tetramisole	Salt	6	Certain
9	Cocaine (70%) + related compounds and tetramisole	Salt	8	High confidence
10	Cocaine (72%) + related compounds, benzocaine and tetramisole	Salt	7	High confidence
4500 Portable instrument				
11	Cocaine (16%) + caffeine	Salt	6	Certain
12	Cocaine (25%) + caffeine	Salt	7	High confidence
13	Cocaine (40%) + caffeine	Salt	7	High confidence
14	Cocaine (50%) + caffeine	Salt	8	High confidence
15	Cocaine (60%) + caffeine	Salt	8	High confidence
16	Cocaine (70%) + caffeine	Salt	8	High confidence
17	Cocaine (16%) + lidocaine	Base	8	High confidence
18	Cocaine (25%) + lidocaine	Salt	8	High confidence
19	Cocaine (40%) + lidocaine	Salt	8	High confidence
20	Cocaine (50%) + lidocaine	Salt	7	High confidence
21	Cocaine (60%) + lidocaine	Salt	8	High confidence
22	Cocaine (70%) + lidocaine	Salt	8	High confidence

Related compounds = methyl ester ecgonidine, methyl ester ecgonine, tropacocaine, benzoylecgonine, trans-cinnamoylcocaine, and norcocaine

*Five replicate measurements for each sample measured by Cary 630 have the same result.

Table. Result summary of 22 seized samples analyzed by the automated IR method. The % cocaine present was measured by the referee chromatography method.

Takeaway: Moving into the realm of mixture analysis, Portable FTIR can with the appropriate model, provide on-the-spot answers to identify illicit components of suspect samples.

NEW – 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

SurveyIR FTIR Microscope Accessory

- User Installable
- USB Powered
- eSpot Video Imaging Software control
- IR sampling modes: reflection, ATR, and transmission
- Illumination modes: transmission, reflection, and oblique
- Variable remote image mask in IR mode
- Manual coarse/fine focus adjust
- Manual transmission condenser focus adjust
- Accommodates a variety of sample mounts and cells

- Simultaneous Sample Viewing / IR Spectrum Collection
- Equal Optical Efficiency in Infrared R/T modes (without compromise)

Specifications:

- 5 mega pixel CMOS color video camera
 - 1900 μ m field of view
- Sample defining masks
 - 2000 μ m, 250 μ m, 200 μ m, 160 μ m, 100 μ m, or 60 μ m *in the specimen plane*
- $\frac{1}{3}$ " minimum working distance, $\frac{1}{2}$ " maximum travel stage z travel
- Manual x, y stage adjust - 1" x 3" standard slide

eSpot™ Video Microscopy Software

The screenshot displays the eSpot software interface. The main window shows a video microscopy image of a fiber with a measurement of 92.33 μm. The interface includes a top-left header with the date and time, a central video frame, and a right-side panel with a thumbnail gallery. The bottom of the interface features a toolbar with various icons for navigation and analysis, and the CziTek logo.

2/27/2016
2:39:19 PM

single fiber - KBr transmission cell

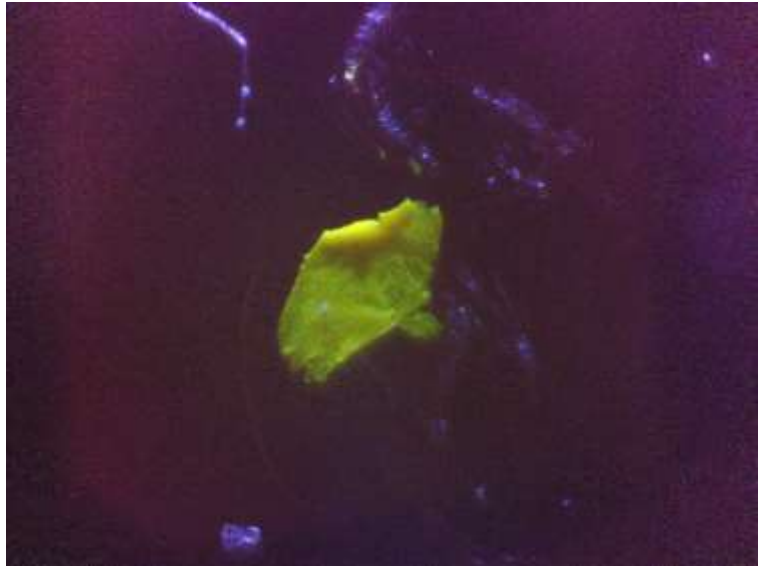
92.33 μm

C:\...fiber on KBr mount 1.jpg

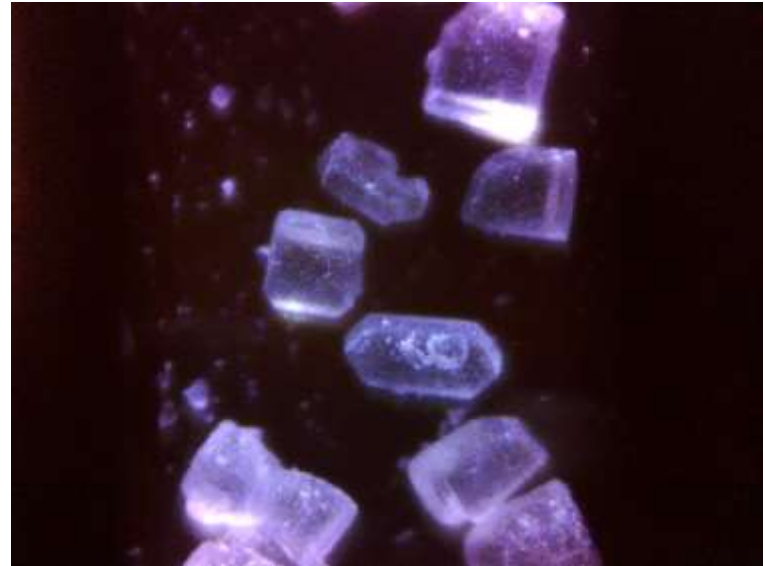
CziTek

Oblique Illumination

Samples viewed with SurveyIR's oblique illumination



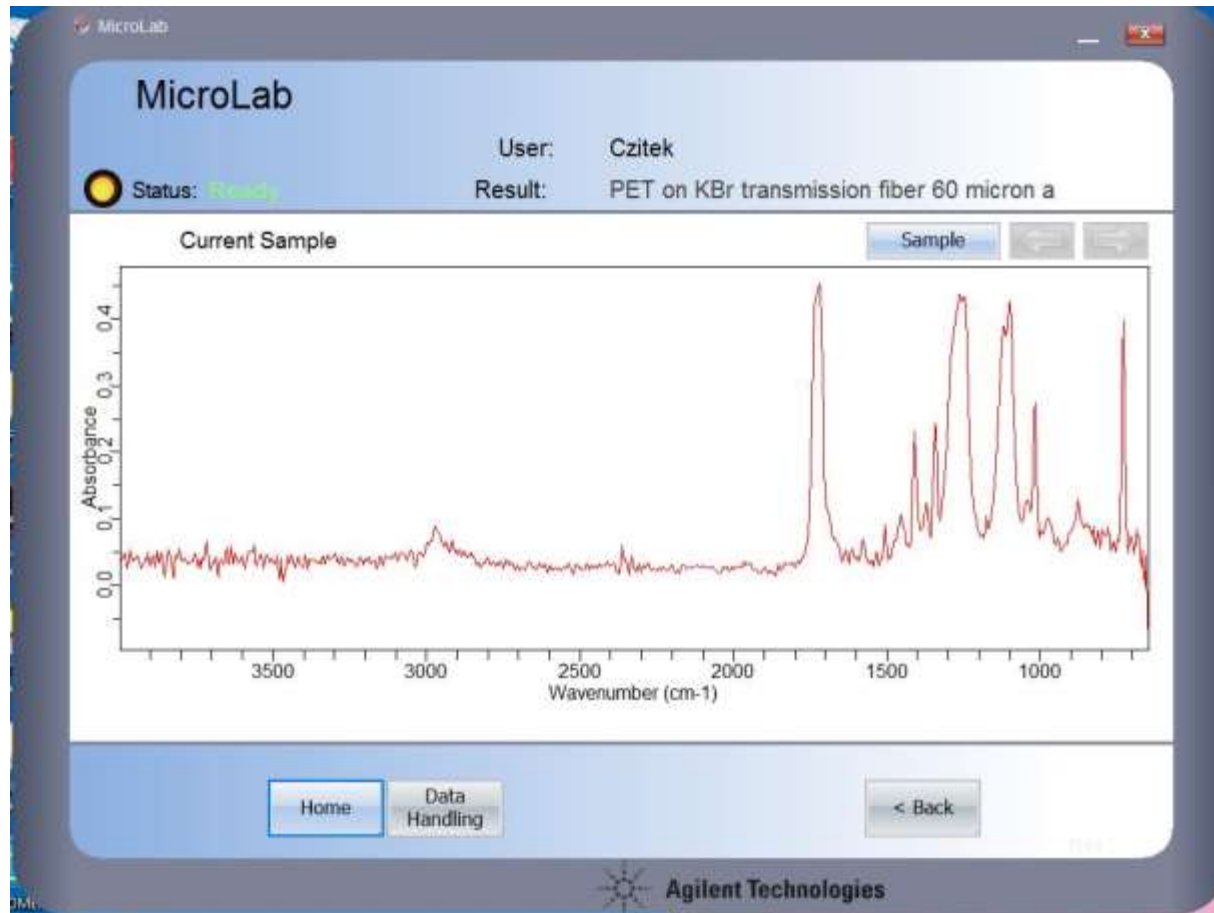
Paint chip



Sucrose crystals through ATR

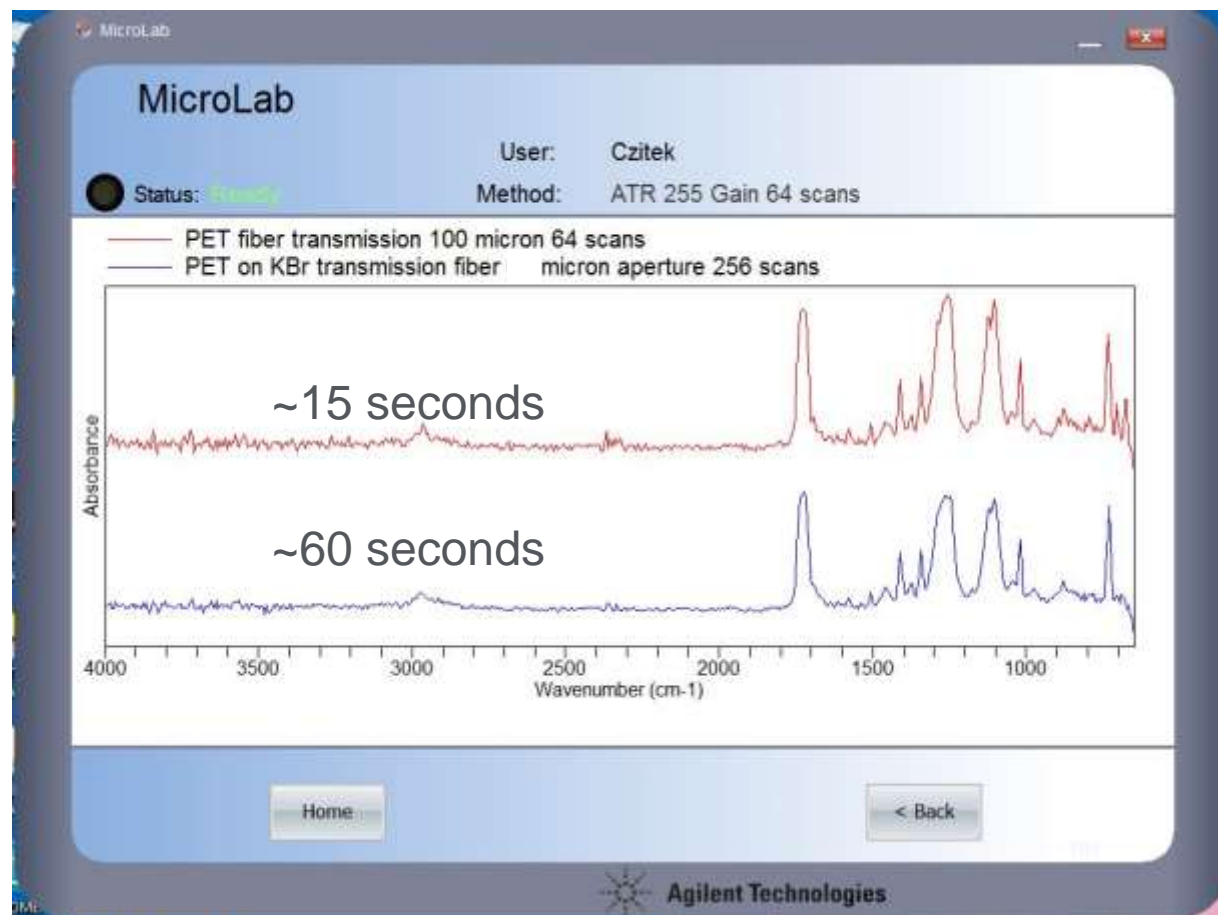
SurveyIR unique oblique visual illumination provide unsurpassed clarity for viewing samples, even through the ATR crystal.

Fibers - Transmission



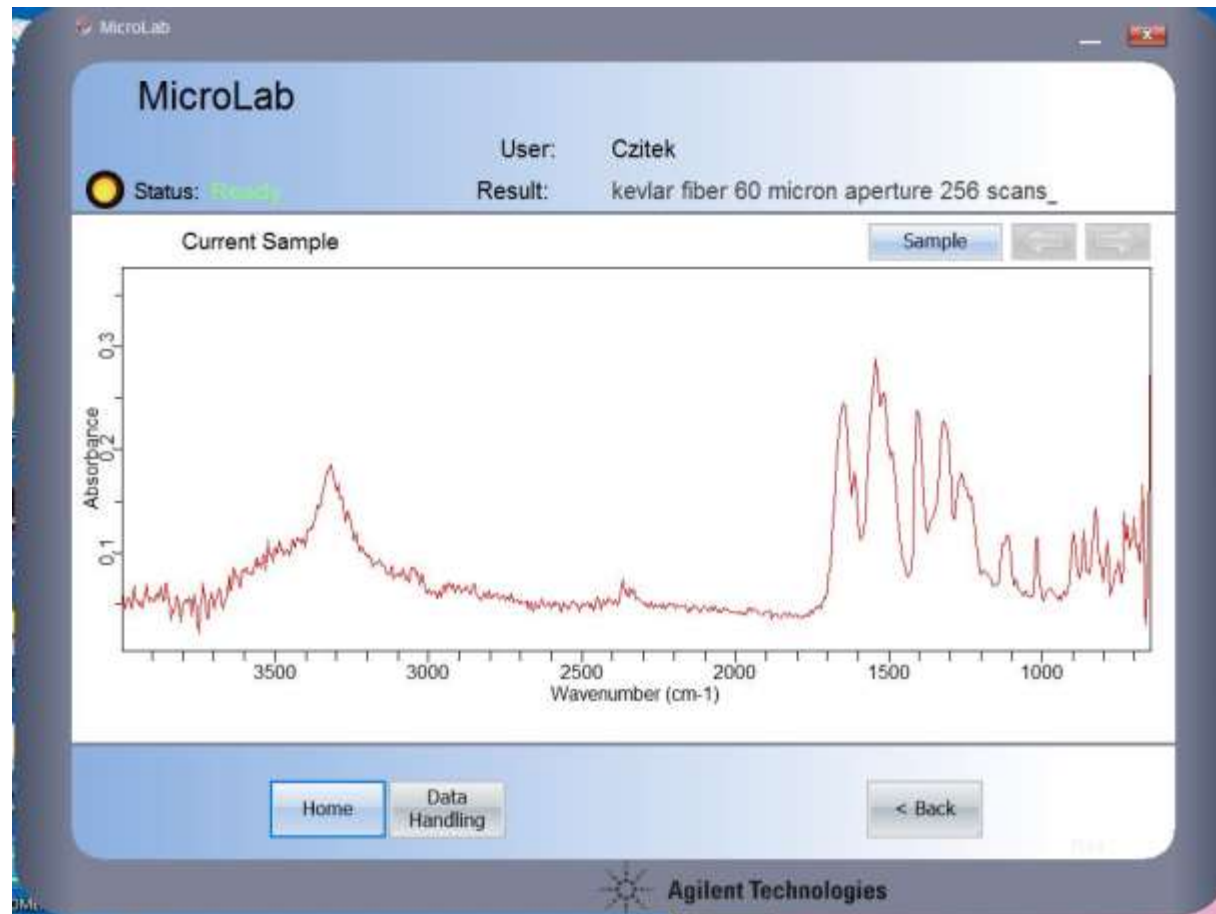
PET fiber
100 μm aperture
256 scans (~1 min)
8 cm^{-1} resolution

Fibers – Transmission collection time comparison



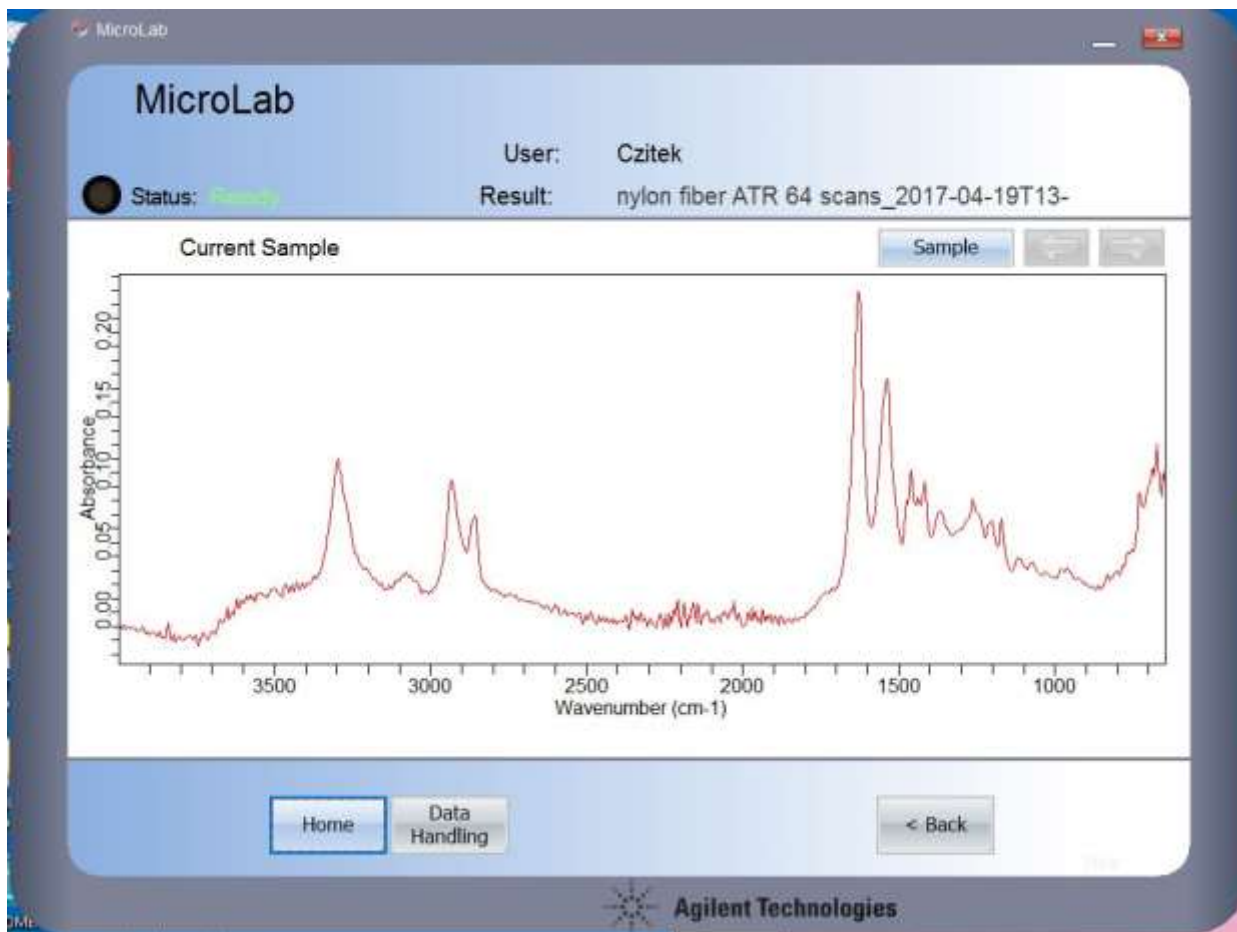
PET fiber
100 μm aperture
8 cm^{-1} resolution

Fibers – Reflectance minimum sample size



Kevlar fiber
60 μm aperture
256 scans
8 cm^{-1} resolution

Fibers – ATR



Before contact

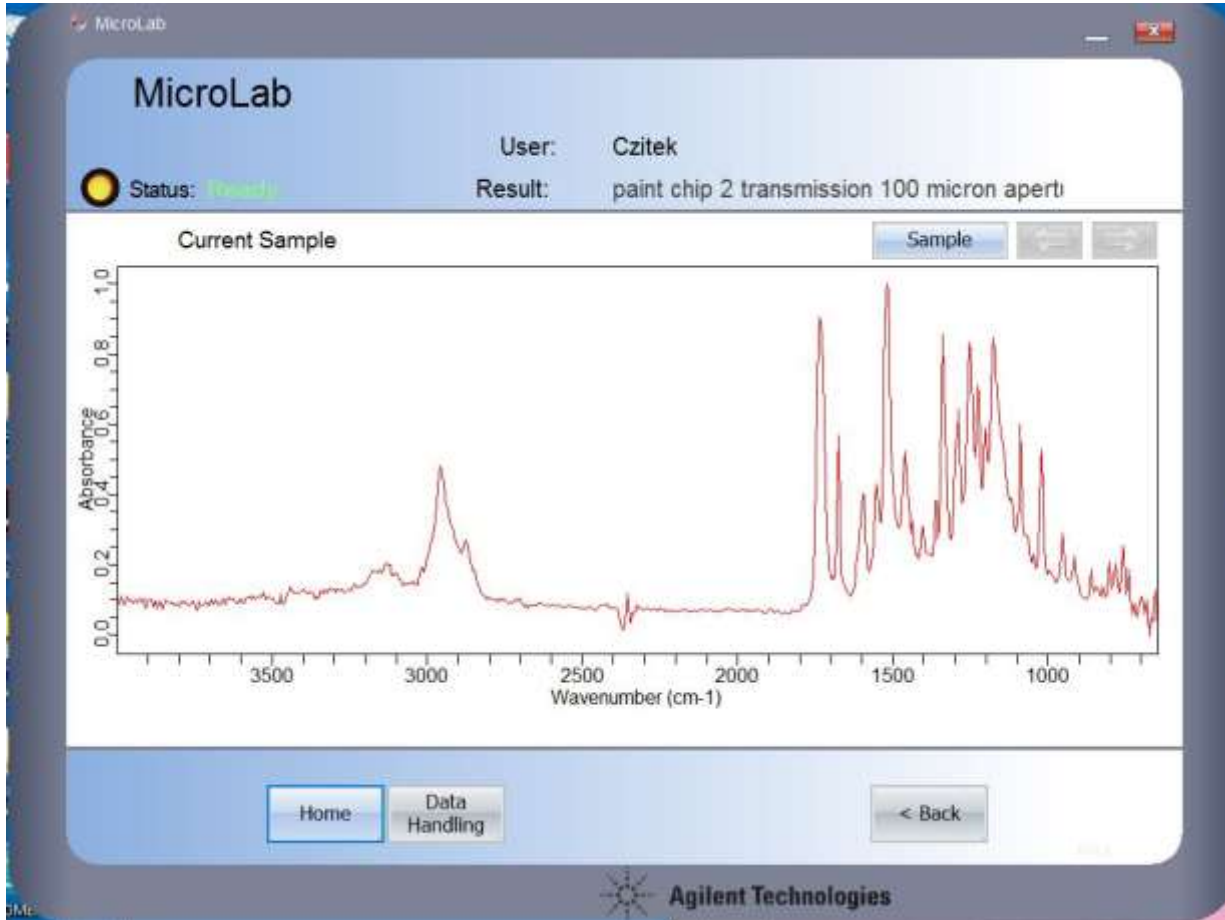


During contact



Nylon fiber
64 scans
8 cm⁻¹ resolution

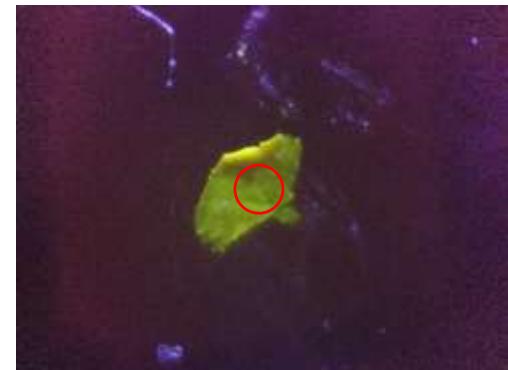
Paint Chip – Transmission



Transmitted Illumination



Oblique Illumination



100 μm aperture
64 scans
8 cm^{-1} resolution

Representative Applications Notes



Automated FT-IR screening method for cocaine identification in seized drug samples

Dipak Mainali and John Seilerlander
Agilent Technologies, USA



Introduction

Quick and presumptive identification of seized drug samples without destroying evidence is necessary for law enforcement officials to control the trafficking and abuse of drugs.

In this study an automated screening method was developed with Agilent's MicroLab software and was used to detect the presence of cocaine in by analyzing the spectra of seized samples that had been measured using an Agilent 630 or 4500 FTIR spectrometer.

The method used the well-established "center of gravity" peak picking mathematical algorithm [1], combined with a conditional reporting feature in the MicroLab software. This automated method could be successfully used by analysts with varying experience levels. The method detected cocaine in a range of chemical mixtures at concentrations as low as 5 wt %.



At-Site Screening and Measurement of Adulterant Levels in Bovine Milk by Mid FTIR Spectroscopy

Application note

Food, QA/QC

Authors

Alan Rain, Ph.D.
Agilent Technologies, Inc.

Professor Luis Rodriguez-Saona
Food Science and Technology
Department of Ohio State University



Introduction

Milk is a common target for adulteration, which is of significant concern to both producers and consumers. Some common milk adulterants include water, whey, sodium hydroxide, urea, melamine and other potentially harmful substances. The purpose of adulterating milk is to artificially increase the volume and/or mask inferior quality product for economic gain.

For this reason, there is significant interest in rapid, easy to use analytical methods that can detect if milk is adulterated and then measure the levels of the adulterants in milk. In a recent publication [1], researchers measured adulterants in milk in the laboratory using the Agilent Cary 630 FTIR spectrometer and showed that the mid FTIR system is superior to NIR spectroscopy for these determinations.

With the recent availability of easy-to-use, dedicated FTIR analyzers, screening milk for adulteration and then measuring the specific contaminant levels is easier and faster than with traditional analytical methods. These FTIR analyzers are designed for use in at-site production locations by less experienced personnel and thus offer the dairy industry a means to improve productivity.



Representative Applications Notes



Pesticide Authentication by Portable FTIR Spectroscopy

Application note

Food

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Introduction

Counterfeit and illegally sold pesticides are a rapidly growing global problem, which affects food production, the health of farmers and consumers, and the overall environment including beneficial insects and animals. In Europe and the U.S. it is estimated that over a billion dollars in illegal pesticides are sold yearly. In some areas of the world, more than 25% of pesticides are counterfeit.

Counterfeit pesticides are generally classified¹ as: fakes, which contain no biologically active ingredients or are highly diluted or banned pesticides; counterfeits, which have packaging that is authentic in appearance but contain impure or incorrect chemicals or illegal imports, which are genetic copies of legitimate products.

There is compelling need to eliminate the trade in illegal pesticides and there are ample rules and regulations, but not enough enforcement. With the increasing availability of mobile and portable analytical instrumentation, those agencies and personnel responsible for ensuring pesticide safety and usage have powerful new tools to address the problem.



Measurement of Acrylamide in Potato Chips by Portable FTIR Analyzers

Application note

Food

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Introduction

Acrylamide is a compound that forms in french fries, potato chips, cereal, bread and coffee when they are fried, roasted or baked. The formation is dependent on cooking conditions, for example, high temperature over-cooking of fried chips results in very high levels of acrylamide. The substance, which forms from the reaction of sugar and amino acids in food, is reported to be a likely human carcinogen and formal regulation of acrylamide levels is under consideration worldwide. The compound is on California's Proposition 65 carcinogenic substances list, which requires a warning label on food products that contain elevated levels of a posted substance. Following legal action by the State of California, major potato chip manufacturers have agreed to reduce the level of acrylamide in potato chips to 2.75 ppb over the next several years. Acrylamide levels are of concern to European Union countries as well, and have been monitored in food for the past two years.



Representative Applications Notes



Agilent Cary 630 Laboratory FTIR and Agilent 4500 Portable FTIR Systems for Detection of Counterfeit Pharmaceuticals

Application Note

Pharmaceutical Testing and Research

Authors

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Introduction

Counterfeit pharmaceuticals are of concern internationally. In certain regions of the world, the percentage of counterfeit pharmaceuticals present in the consumer marketplace is troubling. For this reason, active testing programs are in place, and they tend to rely on classical analysis methods such as chromatography and wet chemistry. These methods can be time-consuming, labor intensive, and typically require samples to be sent to a laboratory for analysis. For these reasons, there is substantial interest in applying optical spectroscopic techniques since they are often faster, require less expertise to execute once a method is developed, and are amenable to use outside traditional laboratories. This latter advantage makes them ideal for screening pharmaceutical samples at points of entry and exit in the consumer supply chain.

This application note demonstrates the effectiveness of Agilent compact and portable FTIR systems for detecting counterfeit pharmaceuticals with three examples: ethambutol hydrochloride, cephalexin axetil, and zirconium calcium.

In a recent article, Bai Ma, et al. compared some optical spectroscopic analyzers as potential solutions for detecting counterfeits of two different, important, and often counterfeited pharmaceuticals [1]. The drugs were ethambutol hydrochloride, an antidiabetic drug, and cephalexin axetil, an antibiotic. Handheld Raman, near-infrared, and portable FTIR analyzers were compared for their potential to detect counterfeiting of these two drugs. The FTIR system used was the Agilent Cary 630 FTIR spectrometer (Figure 1). This application note presents a summary of the researchers' experiments and findings.



Agilent Technologies



Positive Material Identification: Qualification, Composition Verification and Counterfeit Detection of Polymeric Material using Mobile FTIR Spectrometers

Application note

Materials

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Introduction

The progress in the development of advanced materials has resulted in an enormous array of polymer, plastic, composite, and elastomer products, components, and objects. Classes of these materials have similar structure, but small deliberate changes in the formulation cause these compounds to have different use and wear properties. Thus, the development and manufacture of these advanced materials and the commercial objects that are created from them drive the need for analytical methods and technology that can rapidly qualify and verify composition of these materials. Furthermore, with the increased globalization of component sources, ensuring authenticity and detecting counterfeit, mislabeled or out-of-specification polymeric material and components is critical.



Agilent Technologies

Thank you
Questions

