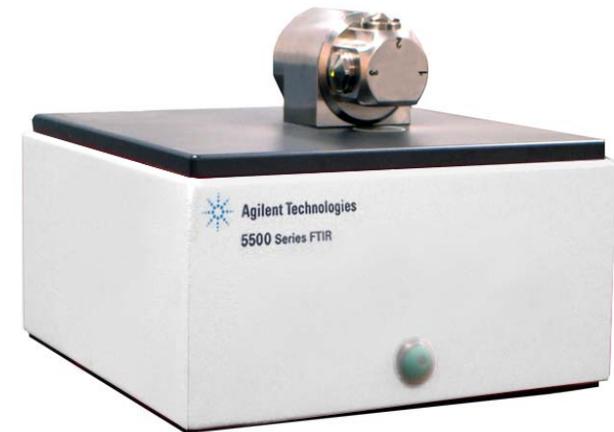


# Hand Held and Portable FTIR Spectroscopic Techniques Investigated to Measure Phthalate Levels in Plastics



By Frank Higgins

# Common Specifications

## *Multiple Instruments from the same engine*

Frequency range

- 4000 – 650  $\text{cm}^{-1}$

Maximum Resolution

- 4  $\text{cm}^{-1}$

Non-hygroscopic optics

- ZnSe beam splitter

Power

- Onboard Lithium Ion Battery

Operating temperature

- 0<sup>0</sup> to 50<sup>0</sup> C

Humidity

- 95% non-condensing



# Hand Held FTIR Products



- 7 lbs
- 7" x 4.7" x 9" inches
- Single Enclosure (optics & electronics)
- PDA Controlled
- Interchangeable sample interfaces



- 4 lbs optical head
- Optical Enclosure wire connected to Electronics
- PDA Controlled
- Dedicated sample interfaces



# 4100 ExoScan Handheld FTIR

## Sampling Flexibility

Liquids & Solids

Smooth surfaces, coatings on metal

Rough surfaces, powders

Smooth flat surfaces, thin coatings on metals



Attenuated Total Reflectance (ATR)



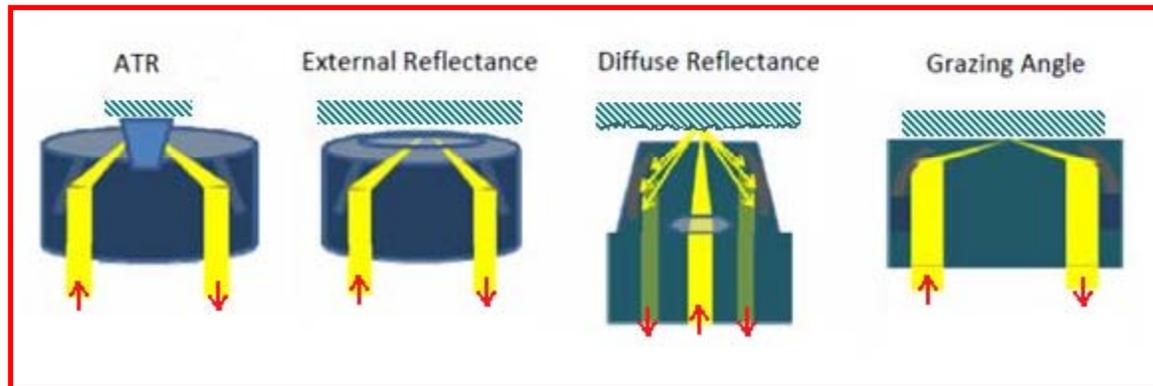
Specular Reflectance



Diffuse Reflectance



Grazing Angle



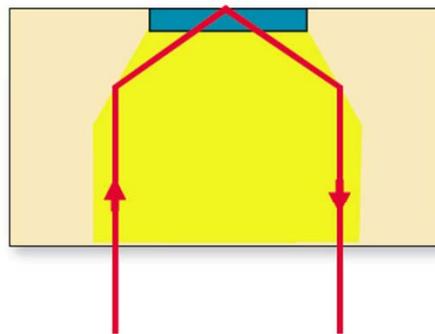
# 4100 ExoScan Handheld FTIR = Versatility



# ML Sample Interfaces: Phthalate Limits

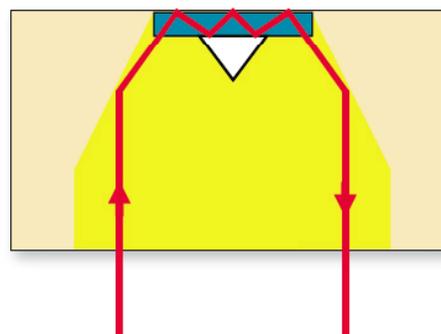
## ATR

- **Single reflection (1 bounce)**
  - Path length  $\sim 2\mu\text{m}$  at  $1700\text{ cm}^{-1}$
  - Solid or liquids
    - Press can be used for Solids
- **Three reflection (3 bounce)**
  - Path length  $\sim 6\mu\text{m}$  at  $1700\text{ cm}^{-1}$
  - Some Solids and Liquids
- **Nine reflection (9 bounce)**
  - Path length  $\sim 18\mu\text{m}$  at  $1700\text{ cm}^{-1}$
  - Some Solids and Liquids
  - Flow cell

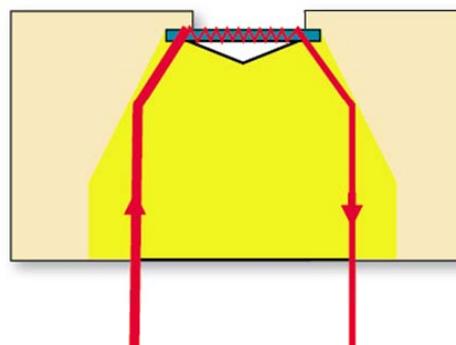


Phthalate Lower  
Limit of Quantitation

1% Total Phthalates



0.1% Total Phthalates

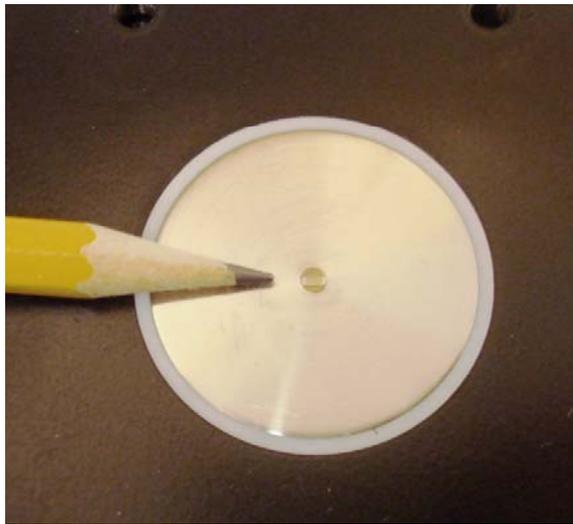


0.05% Total Phthalates

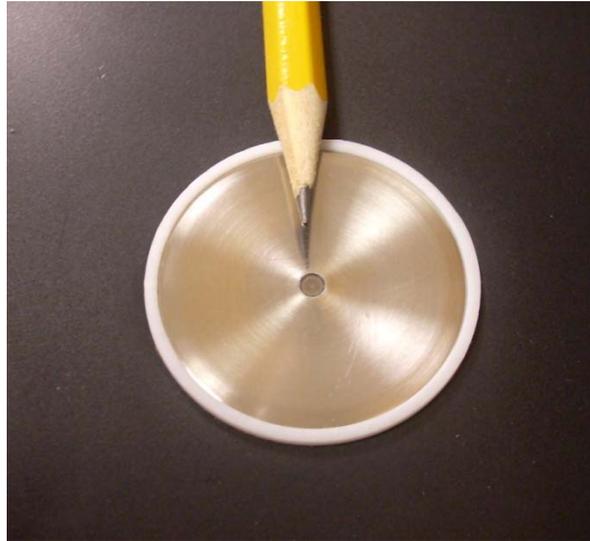


Agilent Technologies

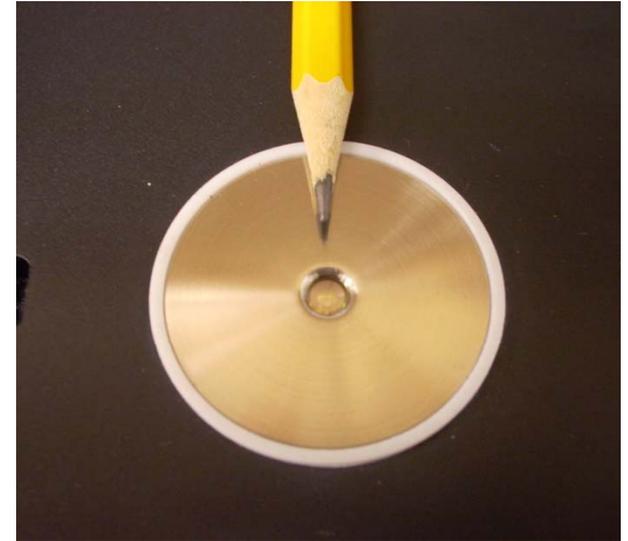
# FTIR Sampling Interfaces: Diamond ATR Equipped on 5500a and 4500a FTIR Spectrometers



Single  
Reflection  
Diamond  
ATR, ~2mm

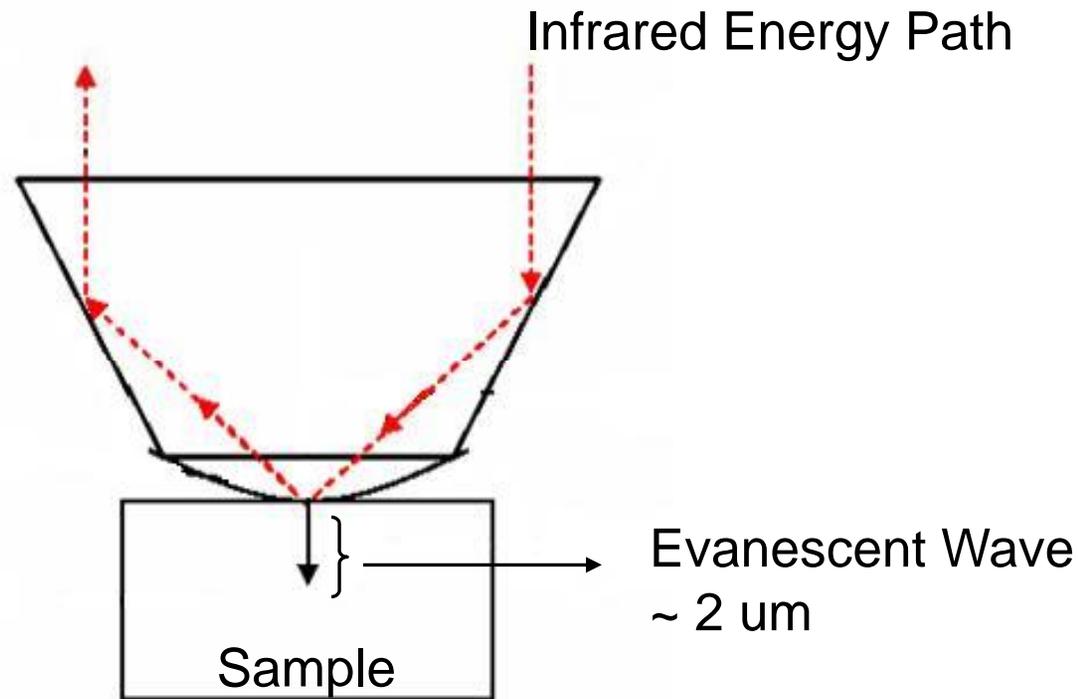


Three  
Reflection  
Diamond  
ATR, ~3mm



Nine  
Reflection  
Diamond  
ATR, ~5mm

# Attenuated Total Reflectance (ATR): Rounded Single Reflectance Diamond ATR



# FTIR Sampling Interfaces: Diamond ATR Equipped on the Exoscan FTIR Spectrometers



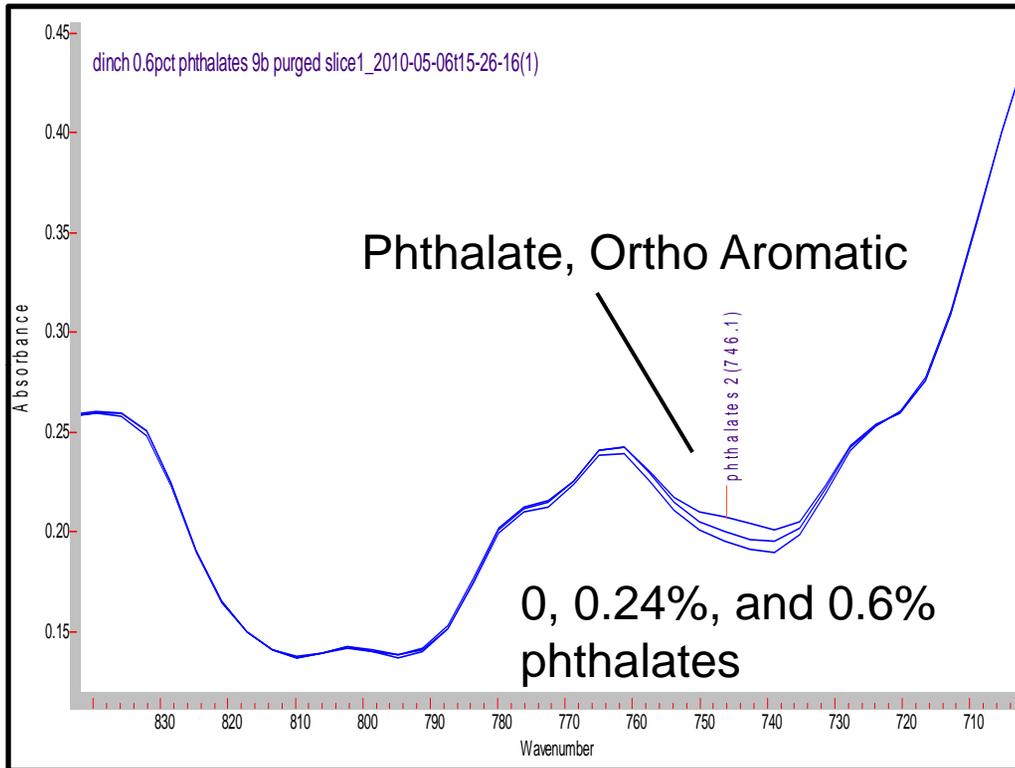
## Single Reflection Rounded Diamond ATR

- Interchangeable attachment or a dedicated (non-removable) interface on the Exoscan
- Fully handheld total phthalates method
- 1% phthalates limit of quantitation

## Possible Future Developments

- 3B diamond ATR Exoscan attachment
  - Realistic 0.1% phthalate LOQ
- Handheld Exoscan ATR Interface optimized for phthalate analysis of plastics
  - Focus on maximizing the number of reflections
  - Similar diamond size as the 3B 4500a

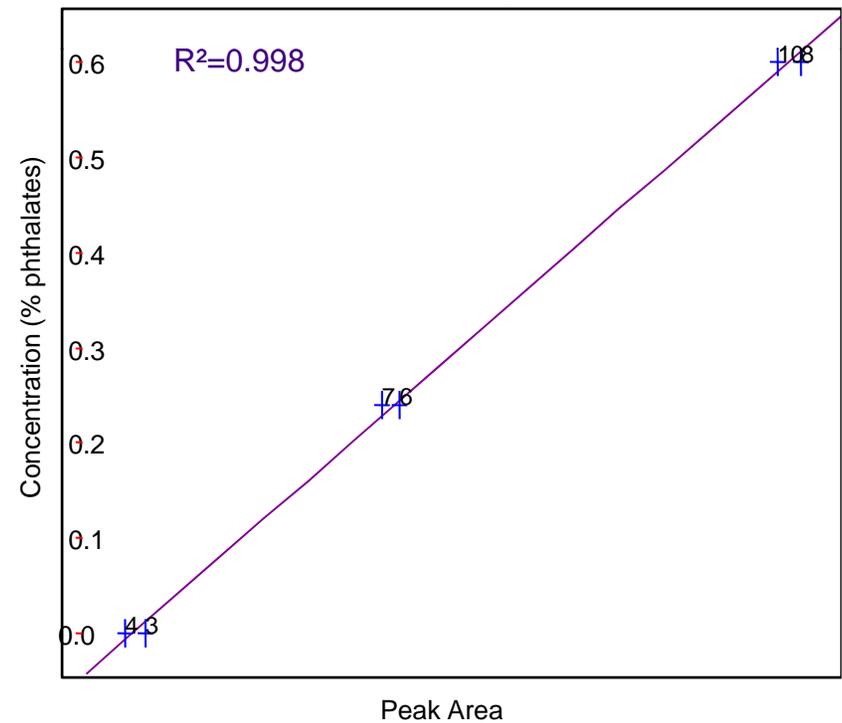
# Phthalates Quantitative Analysis: Nine Bounce Diamond ATR



Analysis with the fully portable 4500a 9B ATR spectrometer



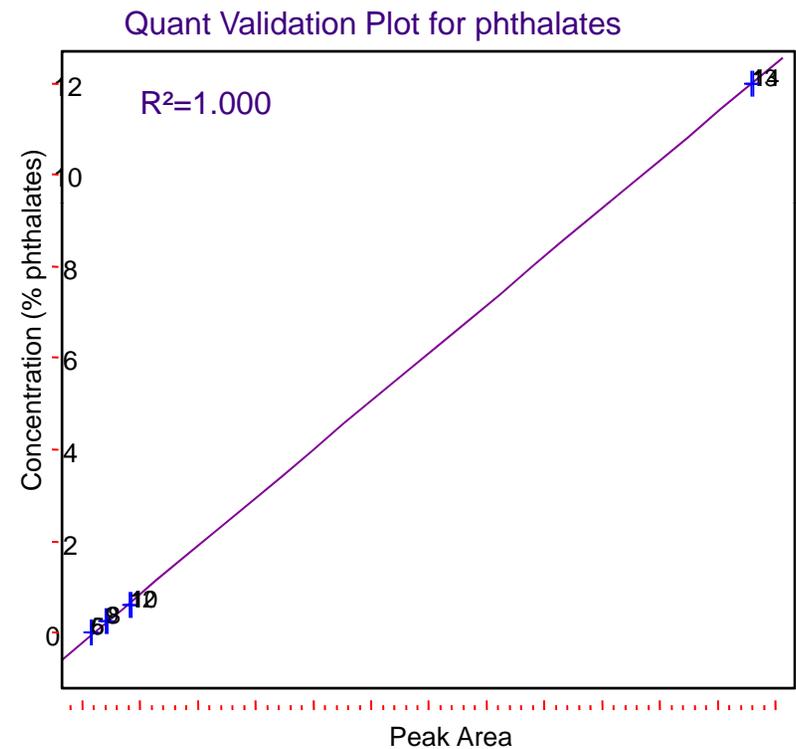
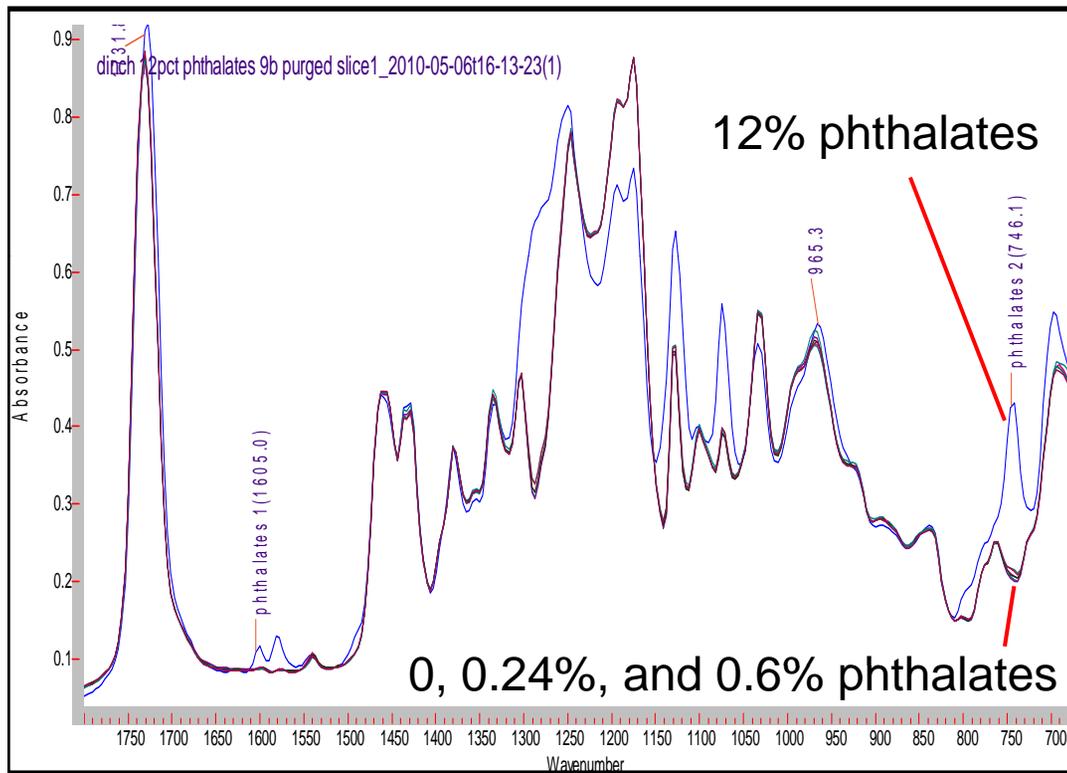
Quant Validation Plot for phthalates



# Phthalates Quantitative Analysis: Nine Bounce Diamond ATR

Large Linear Range for Phthalates

- Multiple calibrations can be used to optimize accuracy



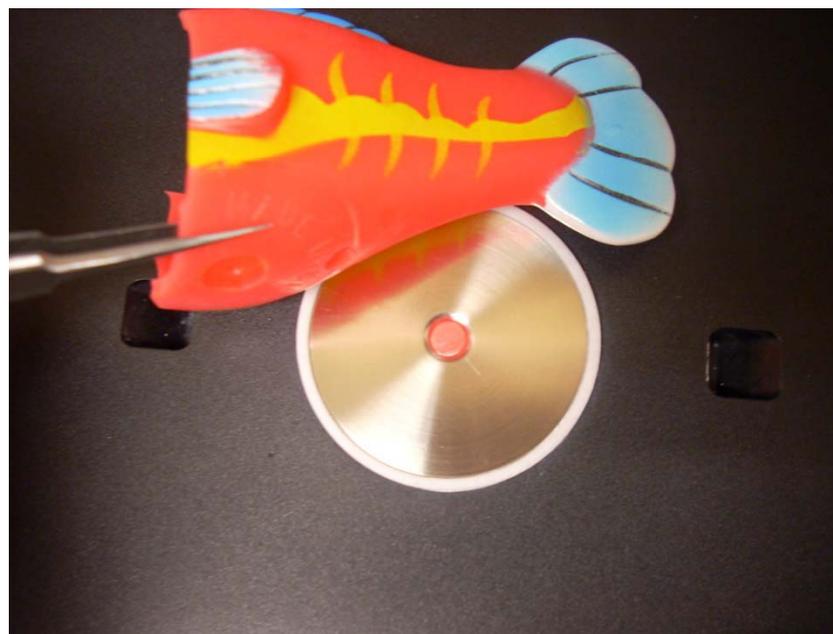
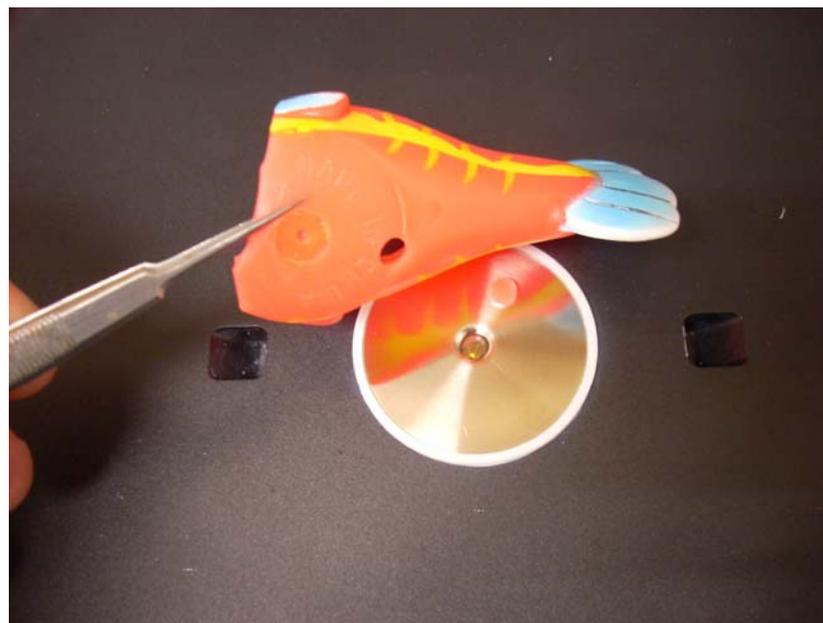
# Phthalates Quantitative Analysis: Nine Bounce Diamond ATR

## Pros

- Limit of Quantitation (LOQ) = 0.05% total phthalates
- No solvents required
- Portable with 4500a FTIR

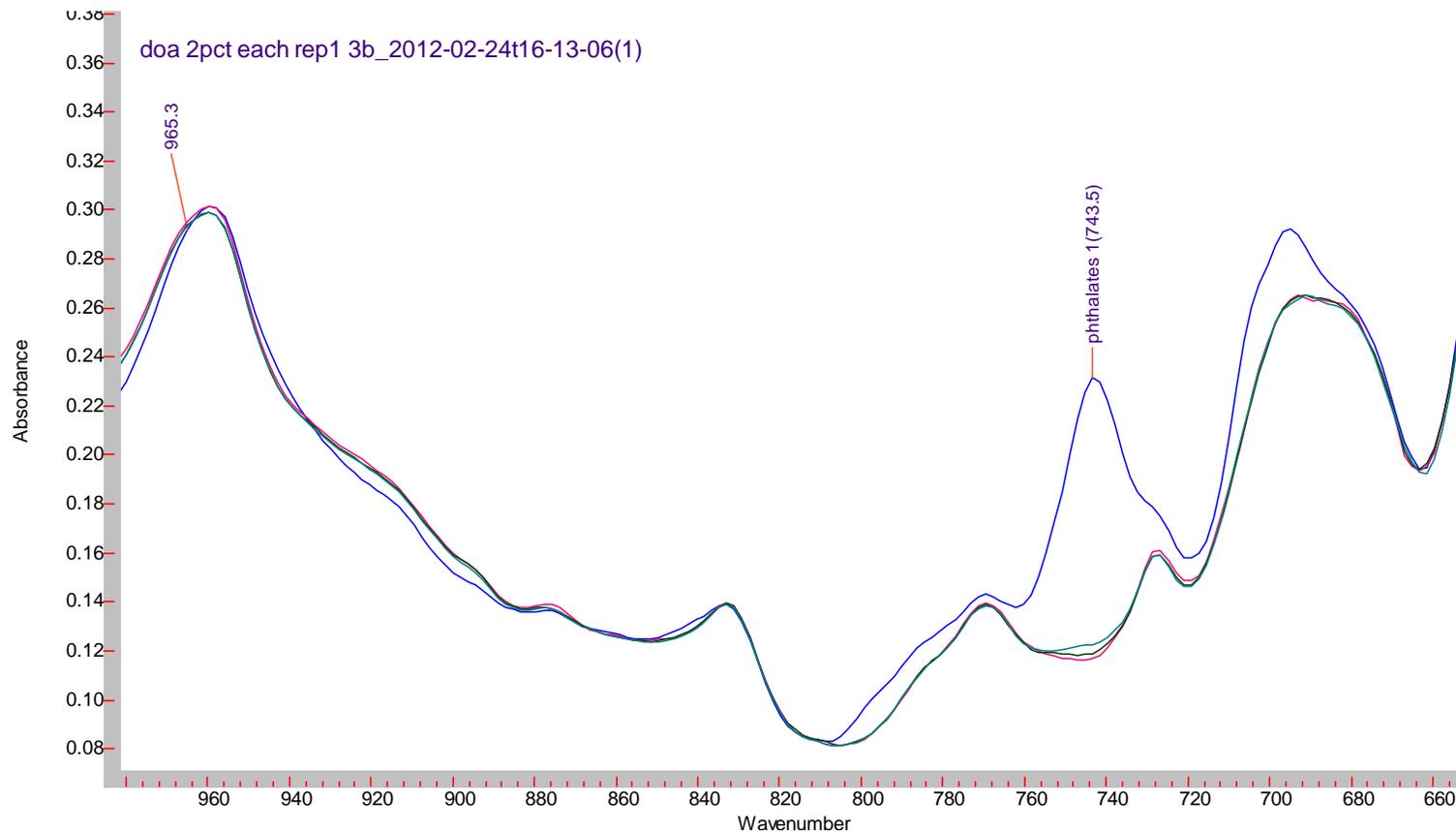
## Cons

- Diamond crystal is recessed
- 5mm diameter sample needs to be punched out
- Sample needs to be pressed flat across the entire diamond surface



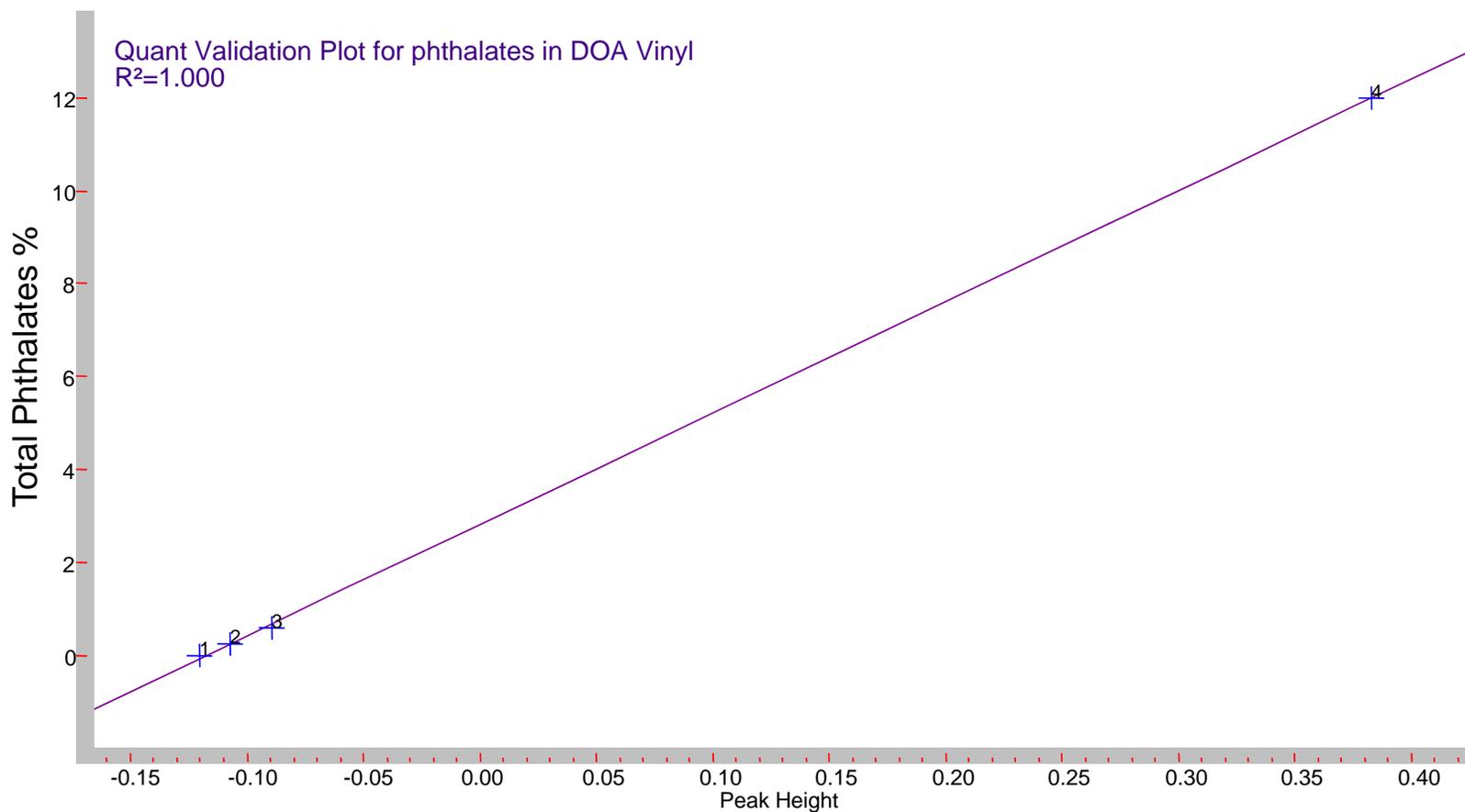
# Phthalates Quantitative Analysis: Three Bounce Diamond ATR

Vinyl plasticized with **DOA** and 0% (Red), 0.24% (Dark Blue), 0.6% (Green), and 12% (Blue) total phthalates. Total phthalates standards (from CPSC) are prepared using equal quantities of DEHP, DBP, BBP, DINP, DIDP, and DNOP.



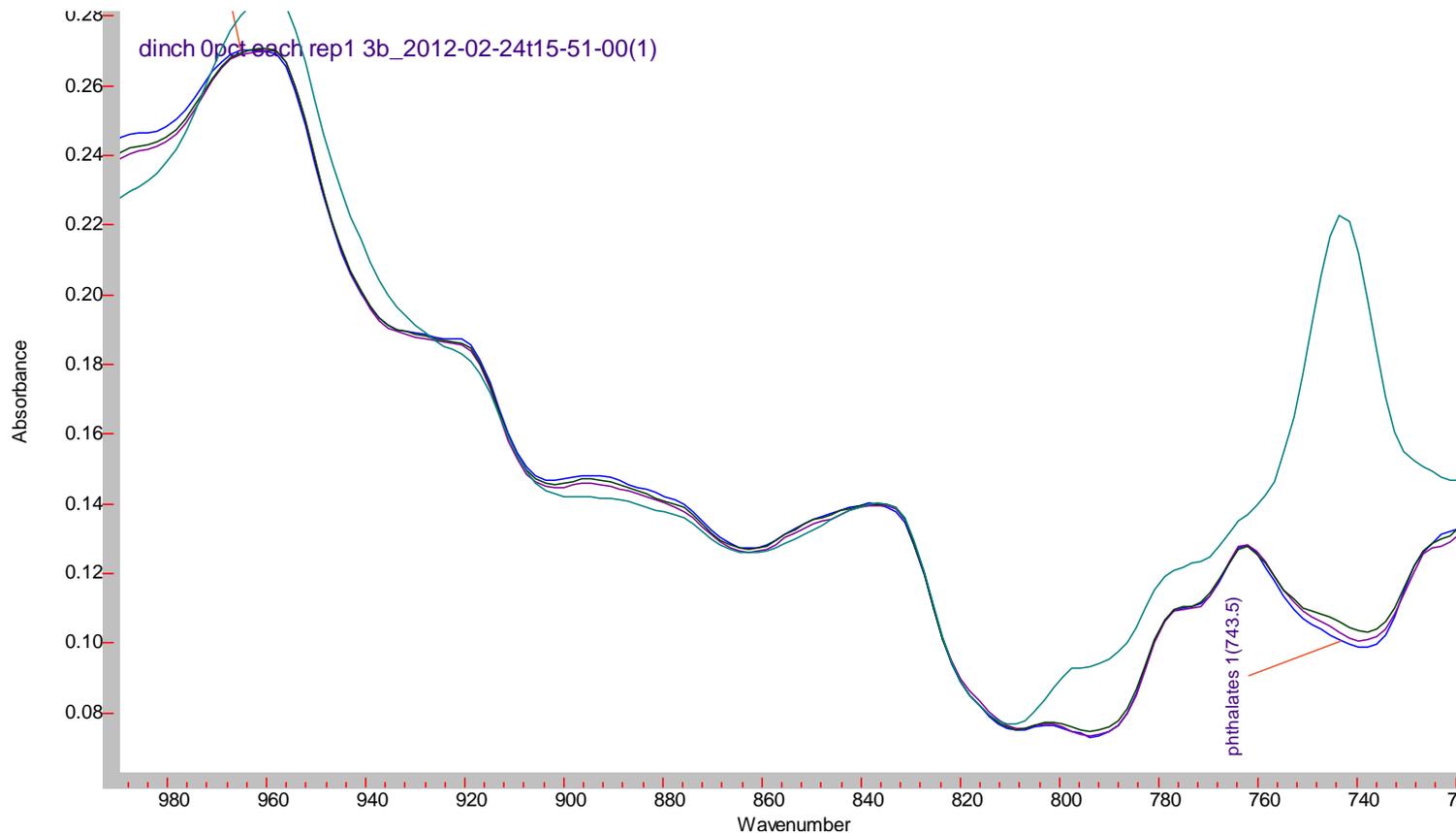
# Phthalates Quantitative Analysis: Three Bounce Diamond ATR

3B ATR calibration for vinyl plasticized with DOA and 0%, 0.24%, 0.6%, and 12% total phthalates.



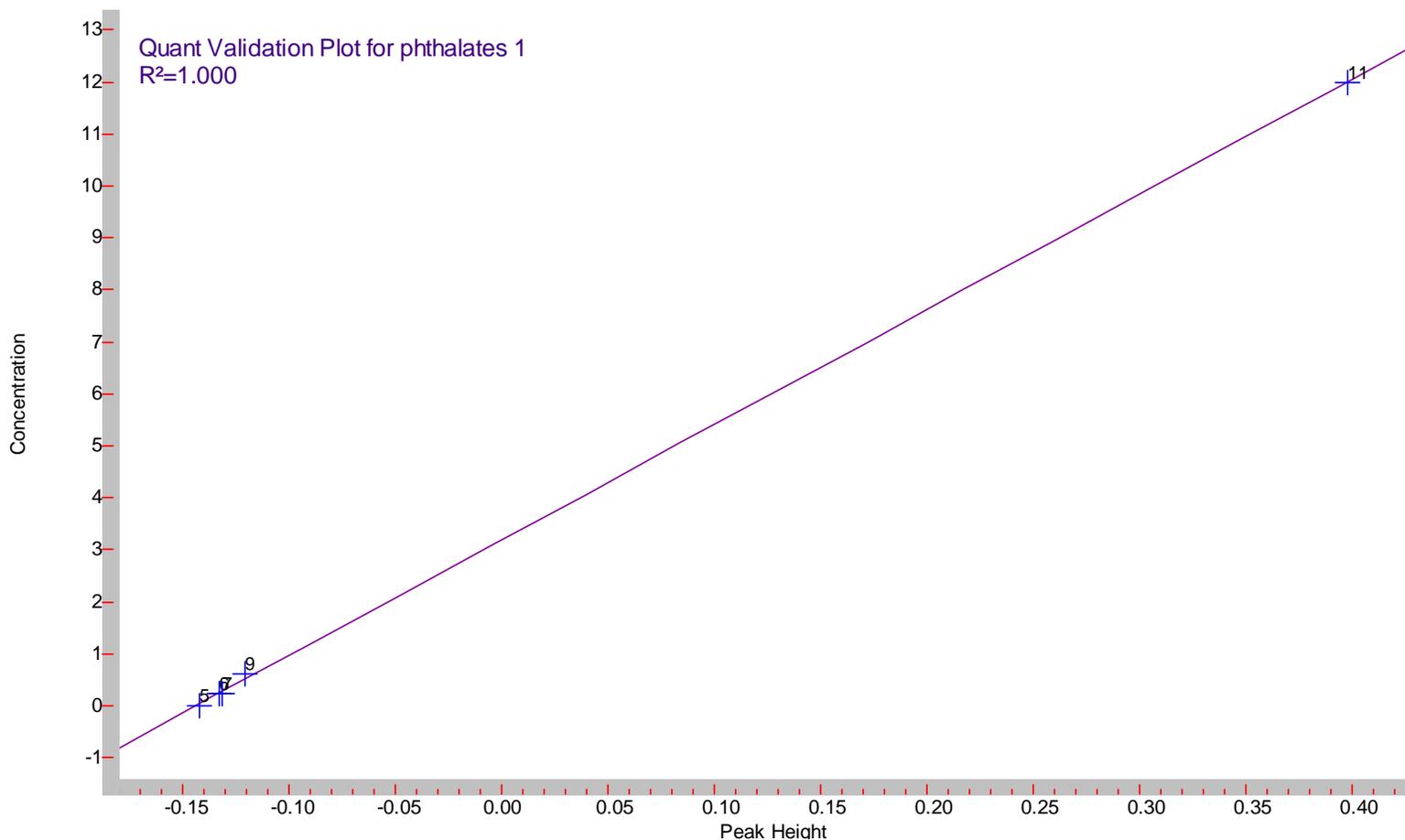
# Phthalates Quantitative Analysis: Three Bounce Diamond ATR

Vinyl plasticized with **DINCH** and 0% (Blue), 0.24% (Maroon), 0.6% (Black), and 12% (Green) total phthalates. Total phthalates CPSC standards are prepared using equal quantities of DEHP, DBP, BBP, DINP, DIDP, and DNOP.



# Phthalates Quantitative Analysis: Three Bounce Diamond ATR

3B ATR calibration for vinyl plasticized with **DINCH** and 0%, 0.24%, 0.6%, and 12% total phthalates.



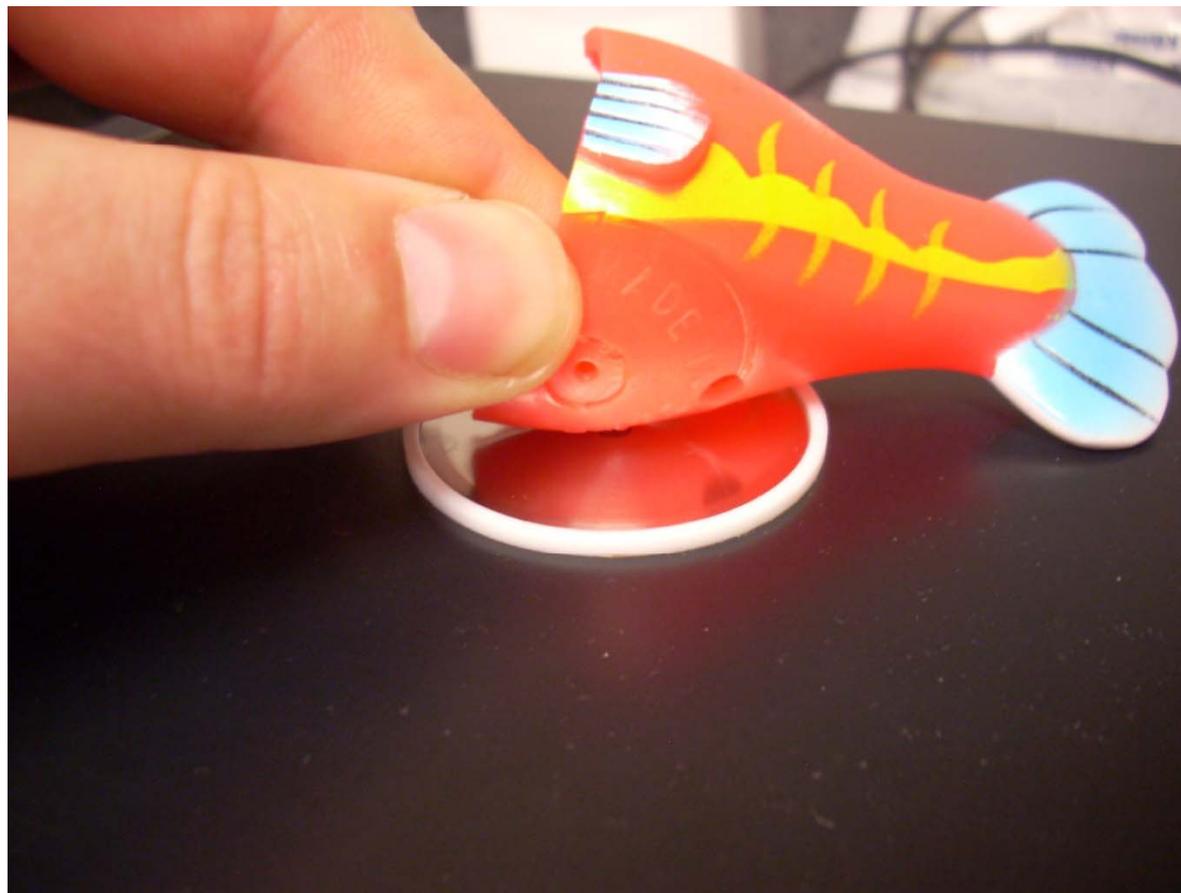
# Phthalates Quantitative Analysis: Three Bounce Diamond ATR

## Pros

- Limit of Quantitation (LOQ) = 0.1% total phthalates
- No solvents required
- Portable with 4500a FTIR
- Non-Destructive, no sample punch-out required
- Diamond ATR crystal is small, ~3mm,
- The slight protrusion of the diamond above the surface is ideal for sampling plastics

## Cons

- Sample needs to be pressed flat across the diamond surface



# Liquids Analysis – On-Site or in the Field



**Agilent Technologies**

## 5500 Series FTIR

- 8 lbs
- 8" x 8" x 4.5"
- External Computer
- External Power
- Dedicated sample interface
- **Designed for mobile/temp. labs**



**Agilent Technologies**

## 4500 Series FTIR

- 15 lbs
- 8" x 11.5" x 7.5"
- Integrated PDA computer
- Internal battery
- Dedicated sample interface
- **Designed for field use**



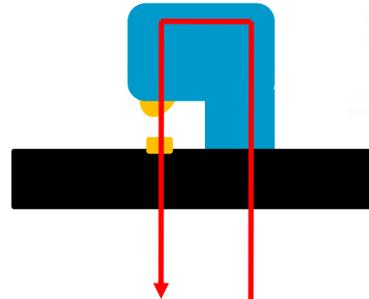
# Liquids Analysis - FTIR Sampling Interfaces

## Single Transmission Cell

- Fixed path length liquid transmission cell
  - Standard 100 $\mu$ m
- Liquids only
- Quantitative analysis
  - 50 ppm to 5 %
- Reproducible and easy to use

## DialPath Transmission Cell

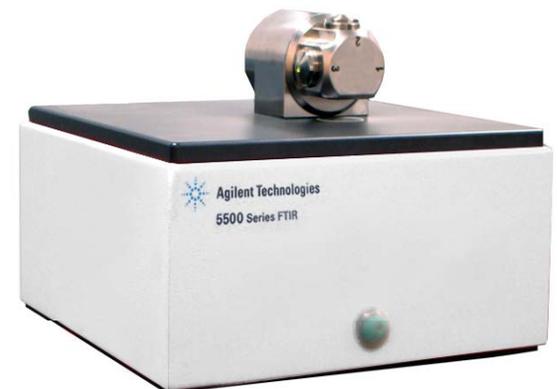
- Fixed, 3 path length liquid transmission cell
- Two Standard configurations
  - Pathlengths of 50, 100, and 200  $\mu$ m
  - Pathlengths of 30, 50, and 100  $\mu$ m
- Liquids only
- Quantitative analysis and Library Search
- 50 ppm to 5 %
- Reproducible and easy to use



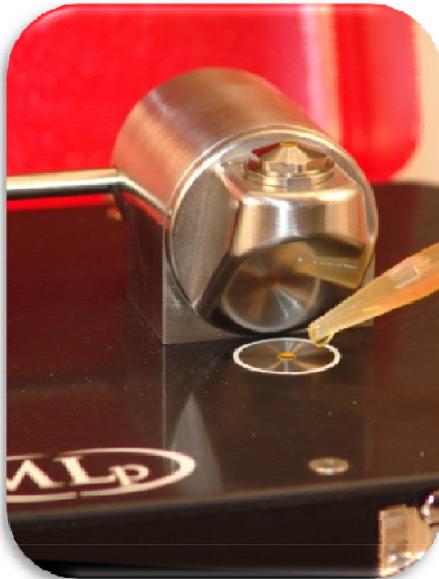
5500t FTIR



5500 DialPath FTIR



# Single Transmission Cell Operation



1. Place Sample on Lower Window



2. Rotate into place



3. Once in place analyze the sample

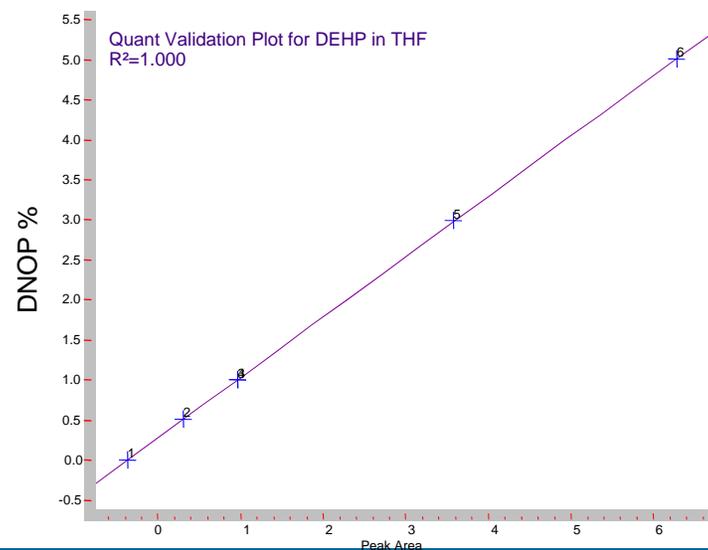
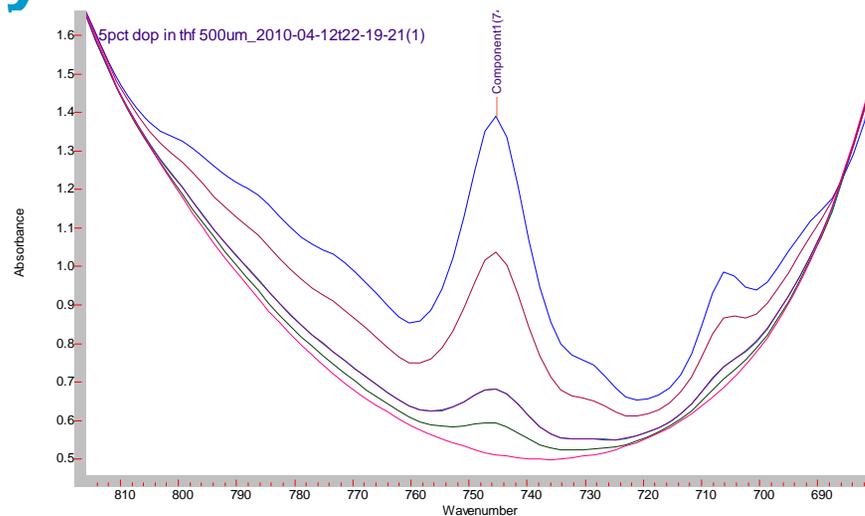


4. Cleaning is easy!

# Phthalates Quantitative Analysis: THF Extraction with FTIR Quantitative Analysis

## Solvent Extraction with Quantitative FTIR

- ❖ Requires a lab
- ❖ Similar sample preparation as the GC/MS method
  - ❖ Accurately Weigh the polymer
  - ❖ Dissolve the polymer in THF
  - ❖ Filter out the polymer
  - ❖ Add the THF to the Dialpath or TumbIR liquid cell
- ❖ Composite total phthalates measurement in 3mins on final solvent extracts
- ❖ FTIR is compatible with many green solvents
- ❖ Easy to clean and no maintenance
- ❖ Dialpath is available with custom pathlengths
  - ❖ 500um ~0.1% total phthalate LOD in THF (0.05g sample in 1mL THF)
  - ❖ 1000um ~0.05% total phthalate LOD



# Advanced Software – Conditional Reporting

Method setup page:  
Conditions with logic  
and limits set

User: admin  
Method: Exoscan - Birds Nests Authenticity

Info	Type	Instrument	Components	Comp Reporting	Custom Fields	Recommend	Reports
<input checked="" type="checkbox"/>	Custom Text	Carbonate 1400	Carbonate 1400	Carbonate 1400 is Value >= 25 AND Carbonate 870 is Value >= 0.5	May contain Calcium Ca		
<input type="checkbox"/>	Value	Carbonate 870	Carbonate 870				
<input checked="" type="checkbox"/>	Custom Text	Feather 1	Feather 1	Feather 1 is Value > 10	May contain feather ma		
<input type="checkbox"/>	Value	MSG 1	MSG 1				
<input type="checkbox"/>	Value	MSG 2	MSG 2				
<input checked="" type="checkbox"/>	Custom Text	MSG Ratio	MSG Ratio	MSG Ratio is Value > 0.6 AND MSG Ratio is Value < 1.5	May contain MSG		
<input checked="" type="checkbox"/>	Custom Text	Sugar	Sugar	Sugar is Value > 10	May contain sucrose		
<input checked="" type="checkbox"/>	Custom Text	salt	salt	salt is Value > 34	May contain salt		
<input checked="" type="checkbox"/>	Custom Text	protein	protein	(Carbonate 1400 is Value < 25 AND Carbonate 870 is Value < 0.5) AND Feather 1 is Value <= 7 AND MSG Ratio is Value > 0.6 AND MSG Ratio is Value < 1.5	Confirmed birds nest		

Up

Down

Edit

Final Result Displayed

User: admin  
Result: In Sugar\_2012-01-19T15-11-47

Results:

Name	Value	Low Threshold	High Threshold
Sugar	May contain sucrose (Critical)		10

# Conclusions

- ❖ Current FTIR portable 3B ATR is capable of measuring total phthalates down to 0.1% in vinyl plastic toys
  - ❖ Sample is pressed onto a 3mm diamond crystal, non-destructive
  - ❖ Other 9B ATR technique can measure down to 0.05% total phthalates but requires destruction of the sample
- ❖ The portable Exoscan can measure total phthalates down to 1%
  - ❖ Sample is pressed onto a rounded diamond ATR, instant contact and non-destructive
  - ❖ Ideal for fast screening of many samples
- ❖ Solvent extraction techniques can be screened by FTIR for immediate measurement
  - ❖ Solvents are measured in long pathlength liquid cells designed for easy cleaning and no maintenance
  - ❖ FTIR prescreening can prevent contaminating the GC/MS system with a dirty sample
- ❖ Advanced software allows for multiple calibrations or conditional limits to be used for a single component measurement – Conditional Reporting