

Technology Review Of Rapid Methods To Detect Counterfeits & Illegal Materials (Findings From Industry Analytical Expert Team.)

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Agenda

- Why Review Technology Now
- Process Used By Team
- Conclusion Of Team
- What Is FTIR/ATR Spectroscopy
- Demonstration Of FTIR/ATR Capability
- Next Steps

Why Review Technology Now

- Counterfeit-and illegal pesticides are entering EU in increasing amounts and are causing threats to farmers, environment and safe food production
- The ability to rapidly detect illegal materials where they are found would help competent authorities to act and create a strong deterrent to criminal activity
- Technology has improved in recent years
- Industry would like to support authorities to find and implement solutions to detect and stop criminal activity with highly regulated pesticides

Two contrasting worlds:

Authorised pesticides

Authorised pesticides are:

➤ **Tested:**

- >100 specific safety tests
- Risks understood, controlled
- Benefits documented

➤ **Authorized:**

- European Commission, Member States, Agencies
- Reviewed every 4-year average review

➤ **Suppliers:**

- Vested in delivering safe, high quality products
- Cooperates with authorities
- Provides stewardship support

Counterfeit and illegal pesticides

Counterfeit* and illegal** :

➤ **Untested:**

- No safety tests
- Unknown Risk
- Possible harm (no benefit)

➤ **Authorized:**

- Unregulated
- Not reviewed

➤ **Suppliers:**

- Criminals
- Unknown to authorities
- No Stewardship
- Support other illegal activities

*Counterfeit – Trick consumer to believe it is authentic

**Illegal – Unregister product, or hidden actives

Industry Expert Team Process

Vision/Objective: Identify the current, low cost, effective technology(s) for rapid detection of illegal, counterfeit and authentic pesticides through objective evaluation of current technology.

- Effective Technology:
 - Assess all compounds in a formulation
 - Identify pesticide(s) in a formulation
 - Identify pesticide in pure samples
- Low cost:
 - Less than \$50,000
 - Commonly found in labs (no cost)
- Rapid:
 - Result < 1 hour
 - Mobile (move to sample)
 - Common

Industry Expert Team Process

(Continued)

Steps for objective assessment.

1. Created a “Technology requirements/attributes” list before suggesting technology

Example of requirements/attributes list items;

- Able to identify hidden actives
- Portable
- Requires little training
- Safety to the operator
- Etc...

2. Add weighting factors to each attribute
3. Identify technologies that might meet requirements
4. Assess and document strengths, weaknesses of each technology
5. Each person rated each technology against the attributes list
6. Discuss and clarify ratings results to ensure accuracy
7. Select primary technology(s)

Attributes & Assessment

Attributes

- On spot analysis
- Portable
- Fast
- Only little training required
- Non-invasive (analysis without opening of sample container)
- No/little sample preparation
- Low costs
- Forgery Proof
- No safety concerns
- No safety problems for user
- yes/no answer without complicated interpretation of measurement results
- usable for any kind of formulation
- now/little maintenance of instrumentation
- Identify hidden materials
- Id and confirm mixtures
- unnecessary to configure/calibrate each instrument
- Single/small sample set needed for calibration
- Calibration electronically shareable with all other instruments
- Share data remotely with Experts
- Accepted by courts
- Accepted by scientist as definitive
- Company does not lose proprietary information
- Multiple vendors without issues
- All organic material
- All inorganic material
- Analysis of Packaging
- First shot analyzer.

Attributes	FTIR/ATR (Diamond)		
	Weighting Factor	Rating Raw (1-10)	Rating Weighted (3-100)
On spot analysis	10	10	100
Portable	10	9	90
Fast	10	9	90
Only little training required	5	9	45
Non-invasive	10	1	10
No/little sample preparation	8	9	72
Low costs	8	8	64
Forgery Proof	10	10	100
No safety concerns	10	10	100
No safety problems for user	10	10	100
yes/no answer	10	10	100
usable for any kind of formulation	10	10	100
now/little maintenance	5	9	45
Etc....
Total	-----	114	1016

Technologies

- Near Infrared (NIR)
- Mid-Infrared (FTIR)
- Raman
- DART MS
- Ion Mobility
- GC (micro)
- LC/UV or DAD
- GC-MS
- LC-MS
- Micro LC
- Cell phone camera
- Image Analysis (Far UV)
- Image Analysis (vis/NIR)
- X-ray Fluorescence (XRF)

FTIR/ATR (diamond)

(Example of Strength/Weakness Assessment)

Strengths

- All organics, many inorganics
- Common technology
- ATR (diamond)
 - allows all liquids and solids
 - Little to no training
- Spectra for library (all instruments produce same spectra)
- Semi-portable instruments exist (desktop, and handhelds with limited abilities)
- Can ID compounds in mixtures
- Can ID pure compounds

Weaknesses

- No separation of compounds
- Not so selective/definitive
- Not able to see low level compounds (much below 1%)
- Id of unknown materials can be masked by other materials.
- Cost is about \$20K
- Open containers

Results

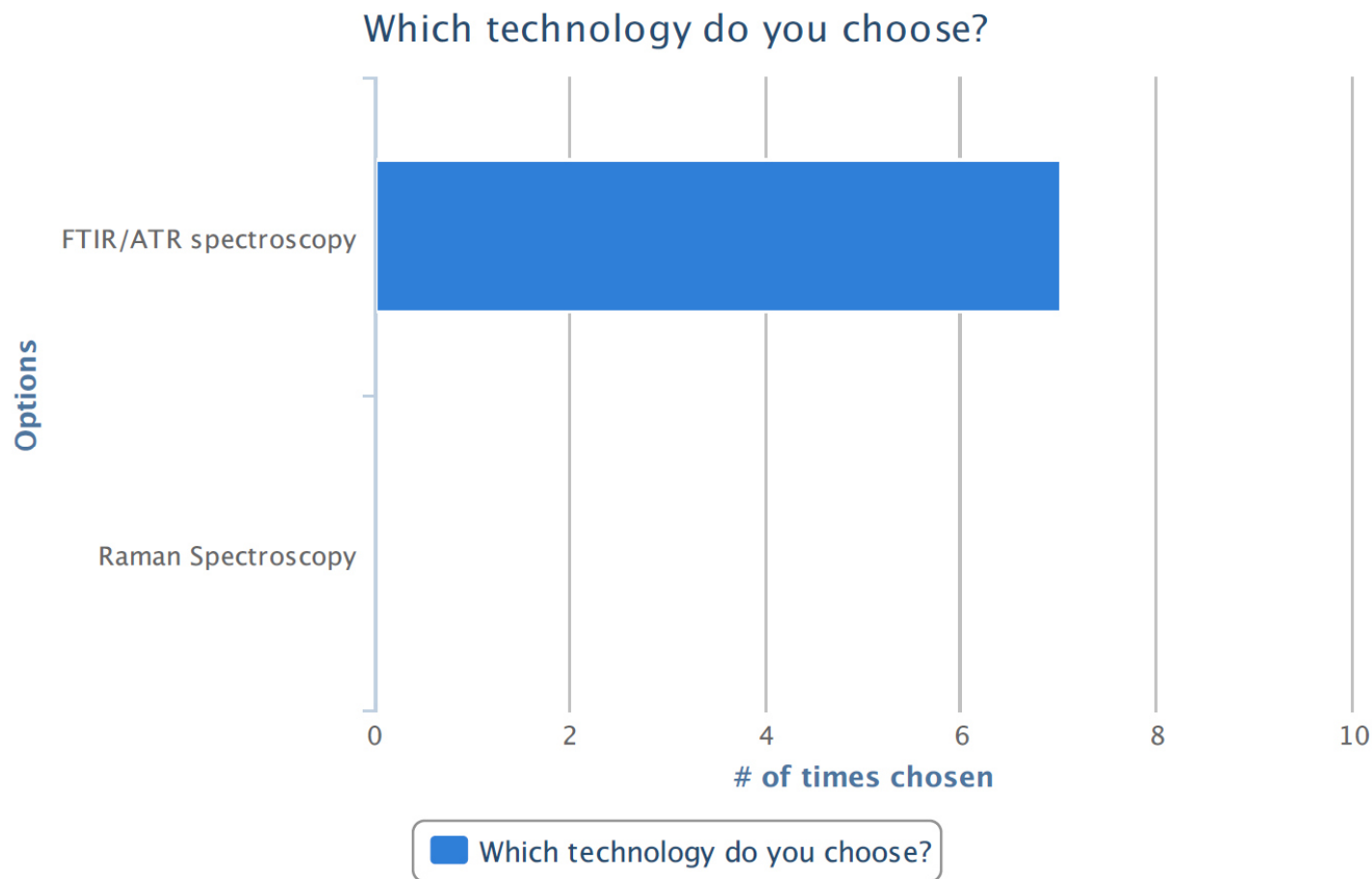
Technology	Rank	Total of all ratings	Guy*	Xiangke	Frank	Freidhelm	John	Christian
FTIR FTIR/ATR (Diamond)	1	7824	1242	1526	1537	1488	1763	1510
Raman	2	7708	0	1526	1597	1552	1627	1406
NIR	3	7496	1050	1490	1537	1312	1715	1442
DART MS	4	6567	0	1525	1350	1177	1248	1267
GC/MS	5	5939	819	1442	1184	1133	982	1198
LC/MS	6	5926	852	1442	1080	1128	1134	1142
Smart phone/camera analysis	7	5239	1027	1348	1220	1363	1308	0
Micro GC on a chip	8	5043	994	1485	1311	1144	1103	
Micro LC	9	4781	946	1469	1064	1136	1112	0
LC/UV or DAD	10	4390	844		1017	1068	1157	1148
Ion Mobility Spectroscopy	11	4028	0	1490	0	1038	1500	
X-Ray Fluorescence	12	4011	1051		1429	1131	1451	0
Image Analysis (near IR)	13	3881	0	1365	0	1194	1322	0
Image Analysis (far UV)	14	3845	0	1365	0	1224	1256	0

Conclusions:

- FTIR/ATR(Diamond) and Raman were too close to call from this data
- FTIR/ATR and Raman were significantly different from others
- Team decided to vote on which to move forward.

*Guys' data was not used because he rated Raman "0". He did this because he did not know enough about it to rate it.

Vote on FTIR versus Raman



Conclusion

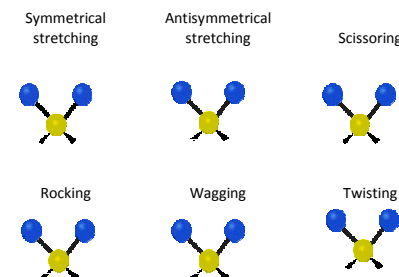
An Industry Analytical Expert team used an objective process to determine the best technology for effectively, rapidly and simultaneously authenticating legitimate pesticides, and for detecting illegal, and counterfeit pesticides when and where they are discovered. From this process, the **Expert team determined FTIR/ATR to be the best technology for this purpose.**

***Because this technology is not specific to Crop Protection products, implementation at borders and ports can be used to detect fakes and illegal activity in other industries.

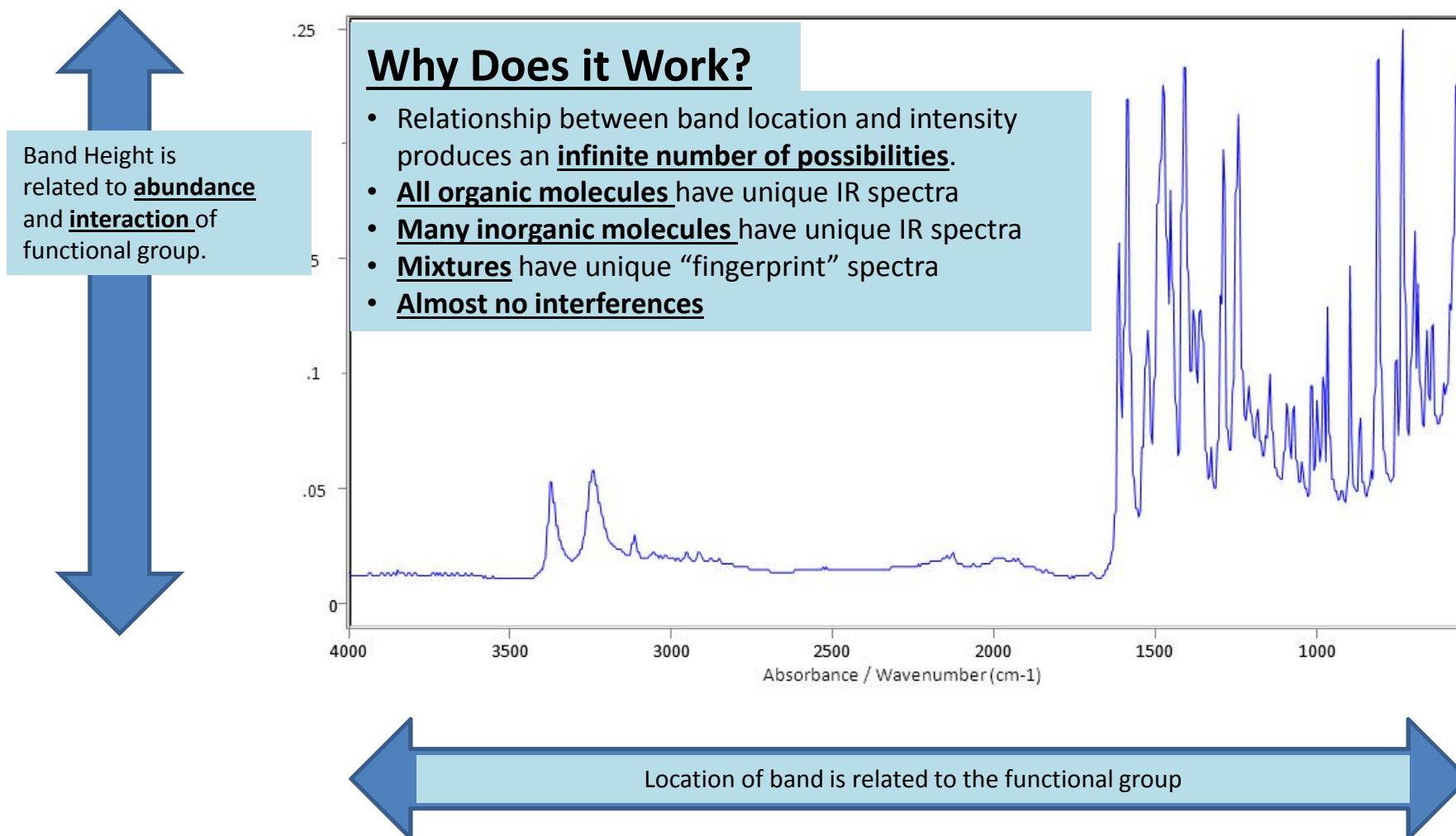
What Is Mid-Infrared Spectroscopy?

- Mid-Infrared Spectroscopy (Mid-IR, **FTIR**) measures the **fundamental vibrations** of covalently bound atoms in molecules.
- Just as one can determine which musical instrument is being played by the sound it makes, each molecule can be identified by the **subtle differences in its vibrational spectrum**.
- It has been well established and **scientifically proven** that the Mid-IR spectra of a compound is **unique** to the compound, and represents a **fundamental, unique property of each compound**.
- This means that if the Mid-IR spectrum of a substance **matches exactly** with that of a known compound it is **conclusive evidence*** that the substance is the compound.

*Good scientific practice is to always confirm a result with at least one other method.

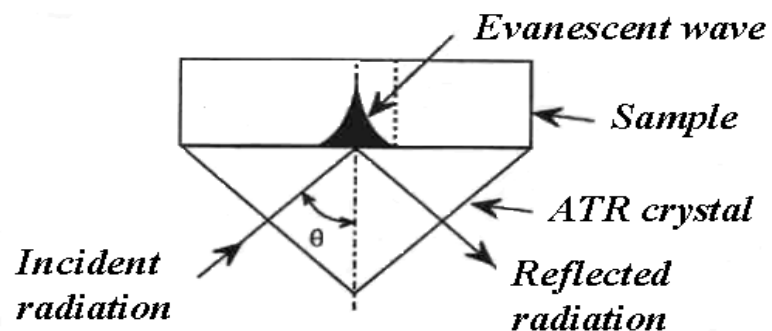


What Does A Mid-IR Spectra Look Like?



The ATR accessory

Attenuated Total Reflection is observed when the sample absorbs internally reflected electromagnetic radiation through interaction with the evanescent wave



This technology allows the analysts to reproduce spectra with a very high degree of precision.

This technology/apparatus is available from all vendors

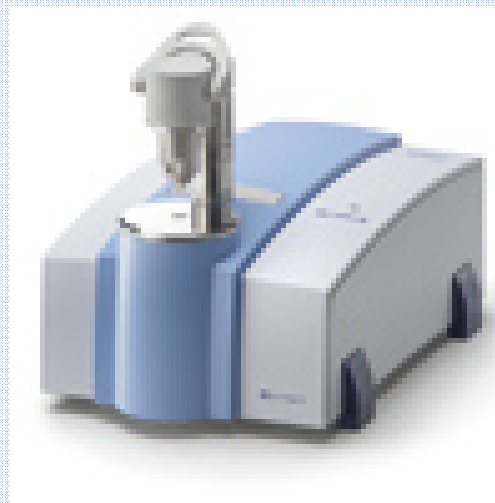
ATR spectral measurement of solids



ATR spectral measurement of liquids

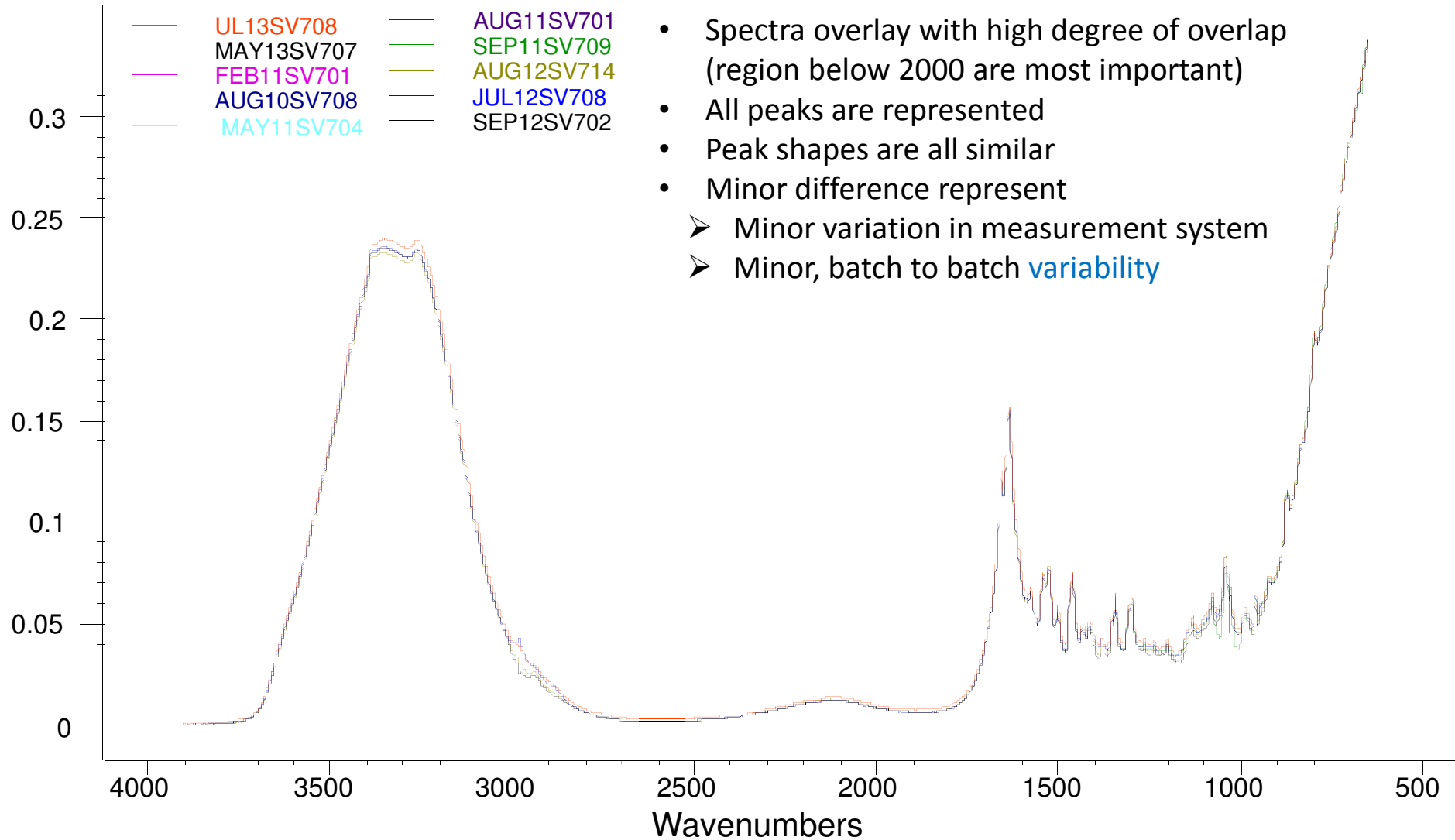


Proven Semi-Portable FTIR Spectrometers



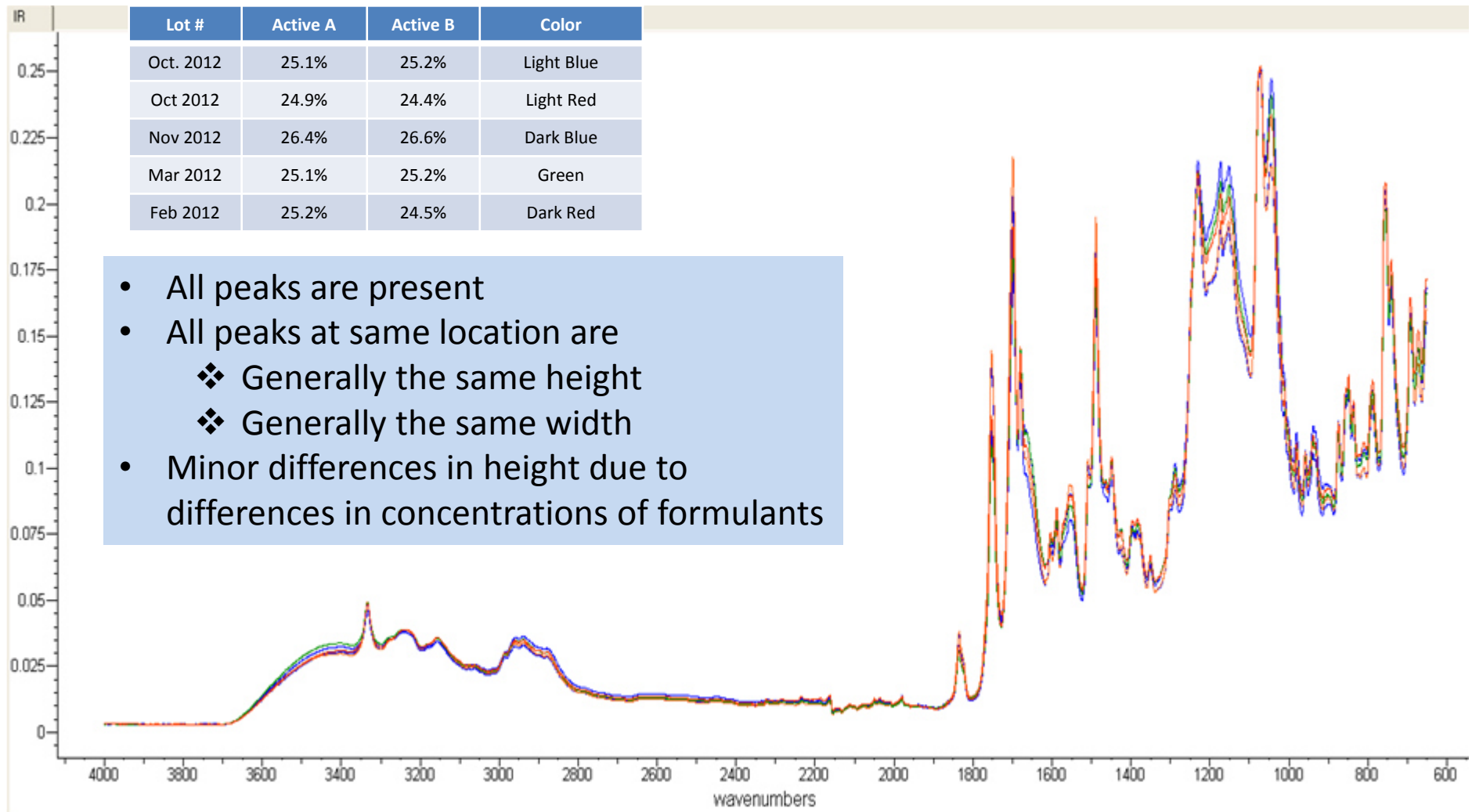
Example of Precision

10 batches of a formulation:



Example of Sensitivity & Precision

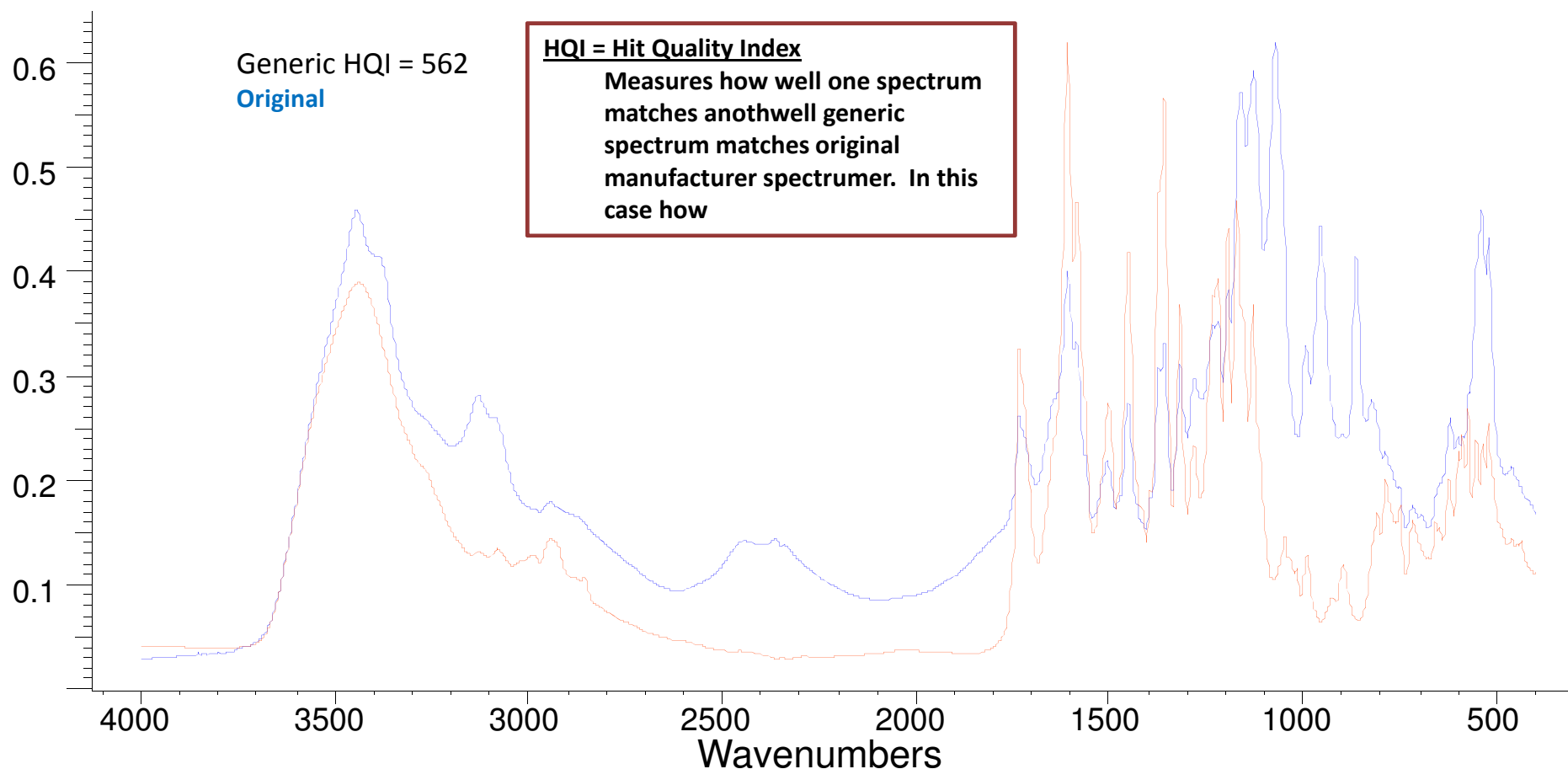
Shows that even with high variation, the spectra still look the same!



Example of original versus Generic

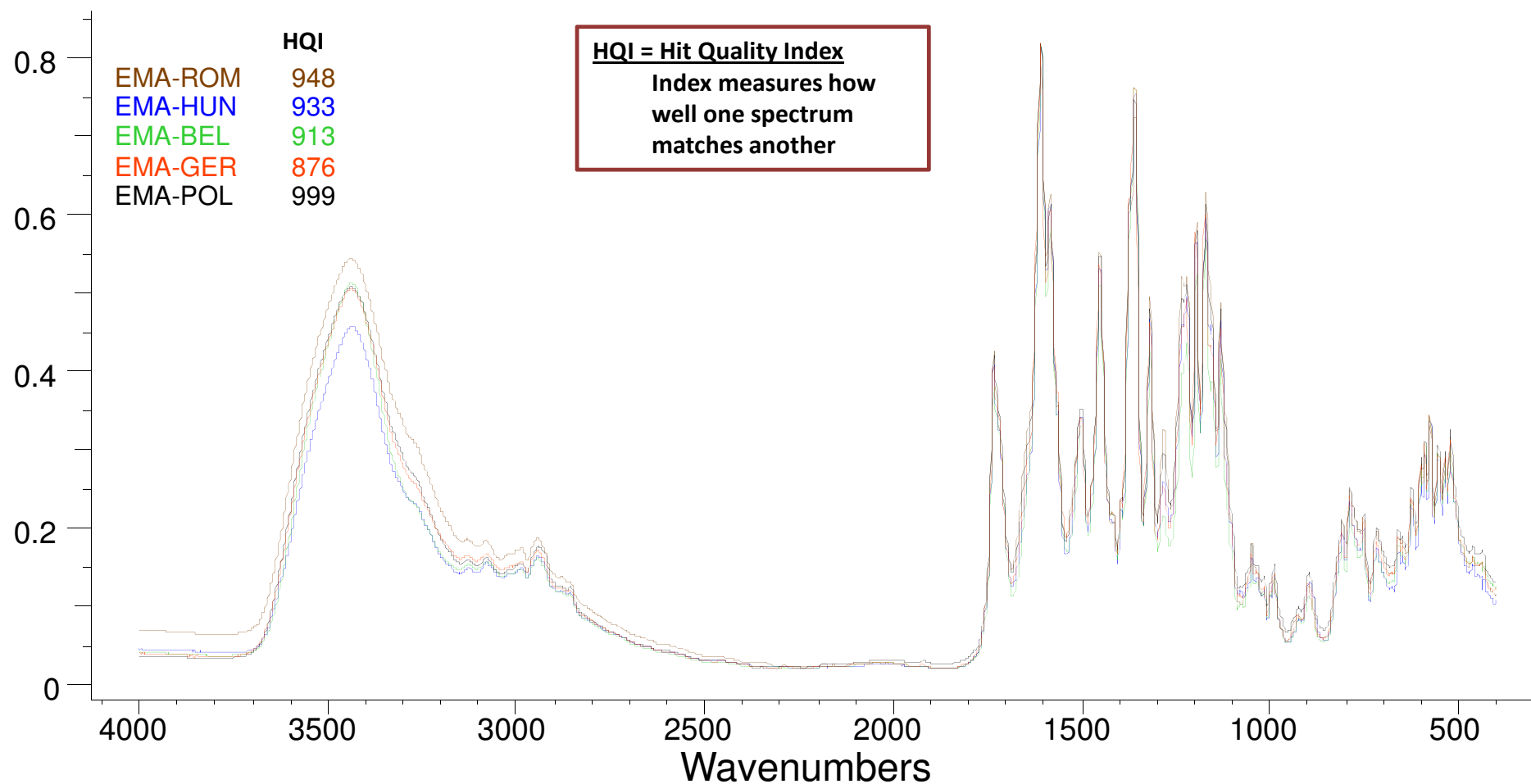
Suspect Rimsulfuron sample from Ukraine

Shows how easy it typically is to see a sample is not the same as another.



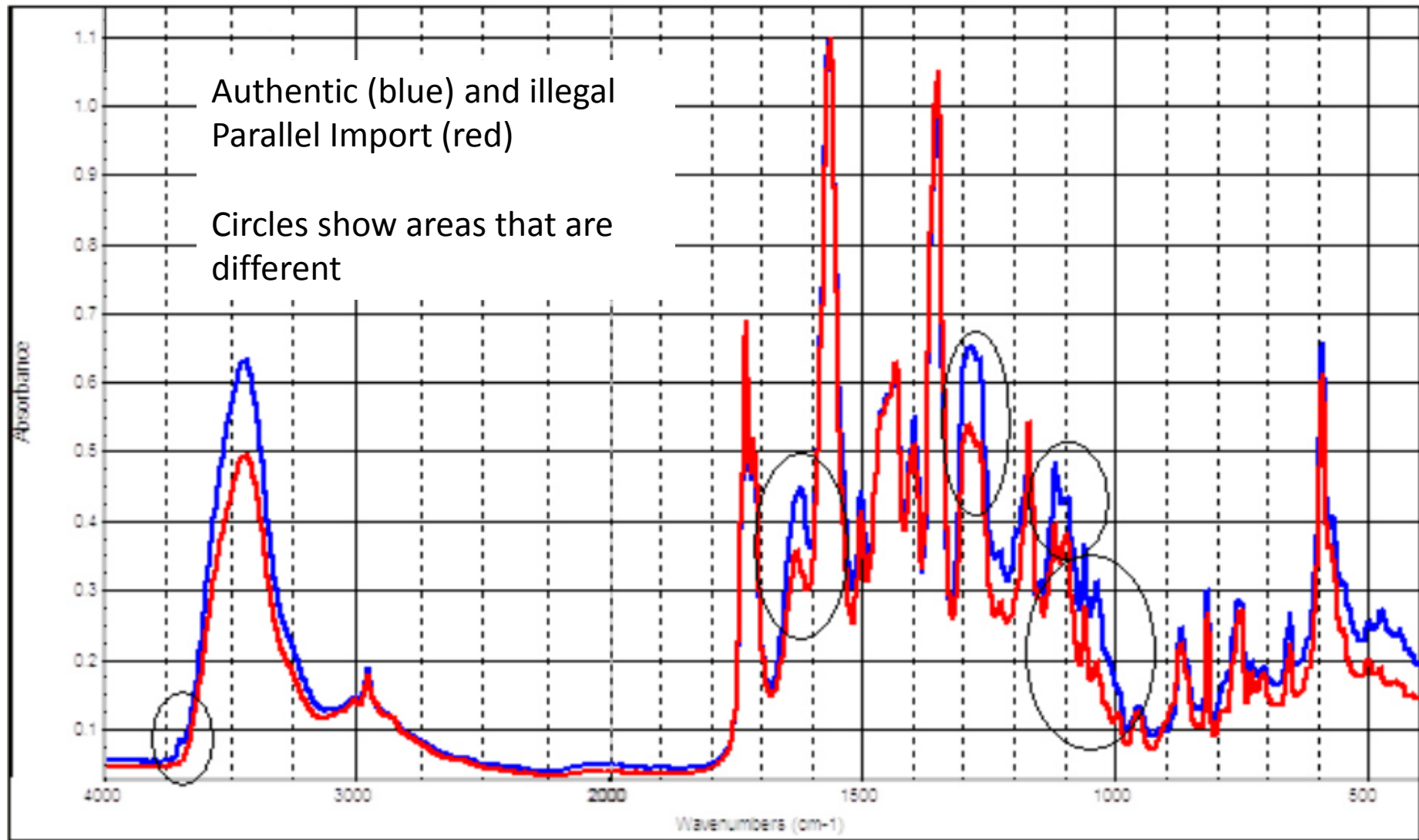
Example of precision & global comparison

Generic Rimsulfuron from several countries



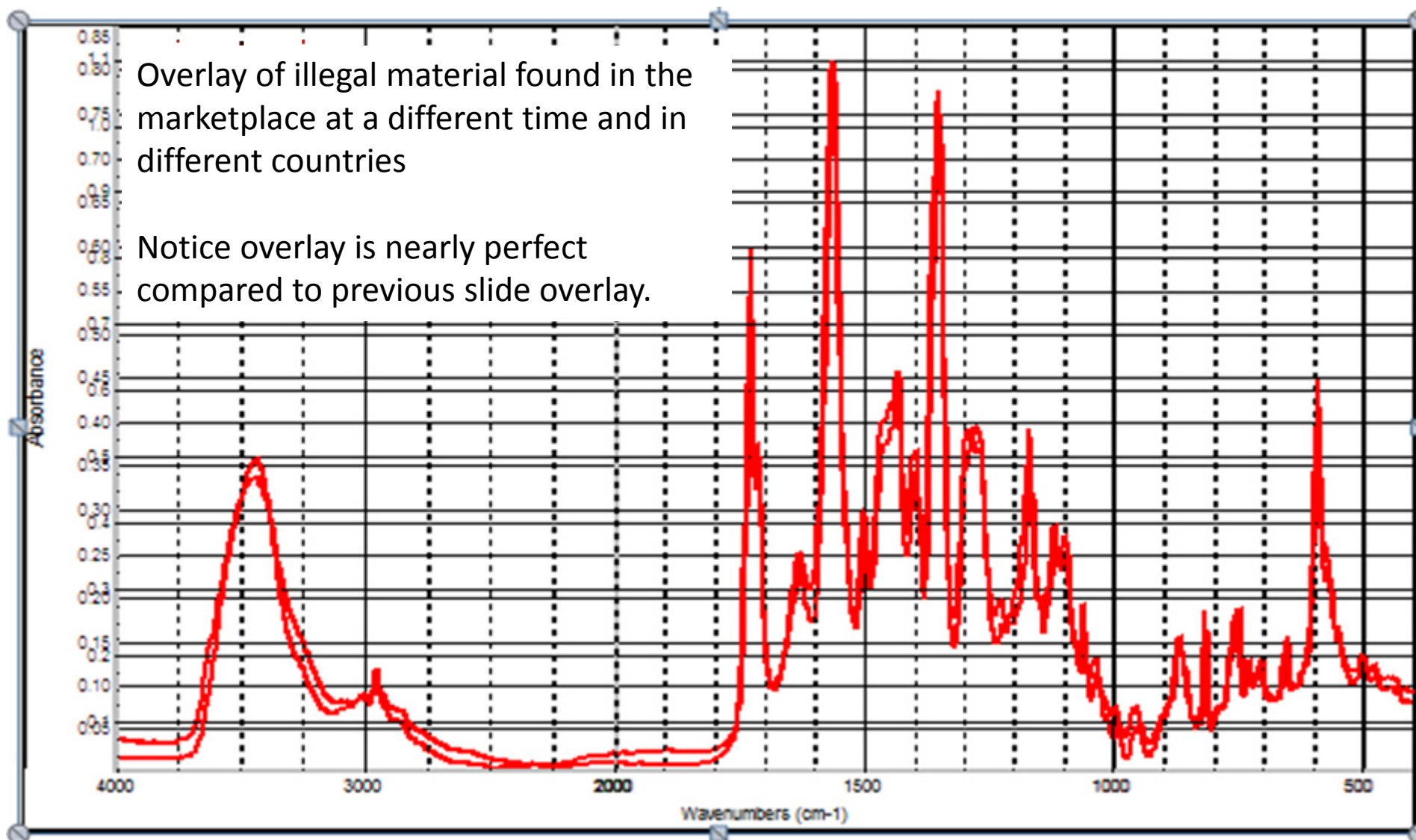
Example Authentic versus illegal parallel

Shows that even minor peaks can show that formulations are different. Peak at about 3,600 wave numbers not in fake, so fake is missing an authentic formulation ingredient.



Example Match Of Fakes

Fake actually matches previously found illegal product. Shows ability to detect networks of criminals across country borders; illustrates international serious organized crime



Questions?