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 classified[1] 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 generic 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.

In this application note, we demonstrate how a portable FTIR spectrometer can be used to rapidly analyze pesticides before distribution, before mixing, and/or before application to crops.

Advantages of Portable FTIR Analyzers for the Analysis of Pesticides

Mobile FTIR offers a number of advantages for personnel involved in ensuring the authenticity of pesticides:

- Mid infrared spectroscopy provides a detailed fingerprint of the chemical structure of the suspect pesticide.
    - Verifies identity of pesticides and identifies diluted, inert, banned or improperly identified agents.
    - Differentiates closely related pesticides based on spectral fingerprint.
- Analysis requires no sample preparation. Results on suspect samples are obtained in less than one minute using the on-board library of pesticides.
    - Large numbers of containers can be rapidly assessed in distribution, warehouse or other locations.
- At site analysis enables personnel to make real-time actionable decisions.
    - Off specification pesticides can be stopped before they are shipped or applied to a field.

The Agilent 4500 FTIR and 5500 FTIR systems (Figures 1a and1b) are well suited to the analysis of pesticides:

- The 4500 FTIR system is fully portable and battery powered. This enables true at-site measurements of pesticides regardless of location.
- The 5500 FTIR system is a bench top system well suited to fixed, at-site labs or in mobile van based labs.
- Both systems utilize an ATR element as the sampling sensor; the diamond sensor is immune to chemical attack by corrosive substances. One drop of pesticide is required for analysis.
- The MicroLab software is intuitive and highly visual. Colored alerts alert the user to the presence of off-specification pesticide.
- The MicroLab software compares the spectrum of the suspect pesticide to spectra contained in an on-board library to instantly verify or disprove identity.

Material and Methods

A series of pesticides were analyzed using the Agilent 4500a portable FTIR system outfitted with single reflection diamond ATR sensor. The pesticides that were analyzed included cis-chlordane, trans-chlordane, aldrin, lindane and campheclor. Approximately 0.5 µL of each pesticide was placed on the diamond ATR sensor. The recorded spectra consisted of 64 co-added interferograms measured at 4 cm^{-1} resolution. Spectra were searched against the a commercially available pesticides library from ST Japan, and the identity of the sample pesticide was determined in less than one minute

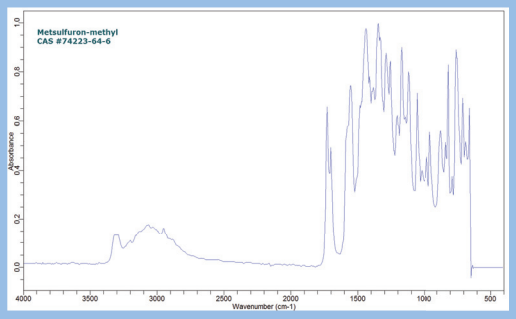
Figure 1a. The Agilent 5500 FTIR analyzer equipped with diamond ATR sampling technology for use in at-site labs.

Figure 1b. The Agilent 4500 battery powered FTIR analyzer for similar measurements in out-of-lab applications.

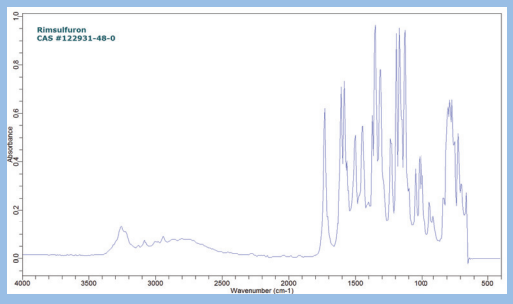
Confirming Pesticide Authenticity is Critical

In 2004, thousands of acres of crops in Spain, Italy and France were destroyed by the application of a counterfeit pesticide. The pesticide was offered at 20% discount and the packaging was identical to that of the expected product. In reality, the 20% discounted substance was metsulfuron-methyl and not the correct pesticide, rimsulfuron. The result was extensive destruction of produce and crops.

Metsulfuron-methyl and rimsulfuron are clearly distinguishable by their mid-infrared spectra.



Spectrum of Metsulfuron-methyl



Spectrum of Rimsulfuron

Portable FTIR aids in ensuring that correct pesticides are applied to fields and produce

Results and Discussions

The pesticides that were selected for this demonstration are banned or severely restricted, as they are classified as persistent organic pollutants. These are all chlorine containing compounds that are toxic to humans and animals, as well as to insects.

Cis and trans chlordane, which have similar structures, were readily identified by their respective spectra and comparison with the commercial pesticide library provided excellent matches (Figures 2, 3)

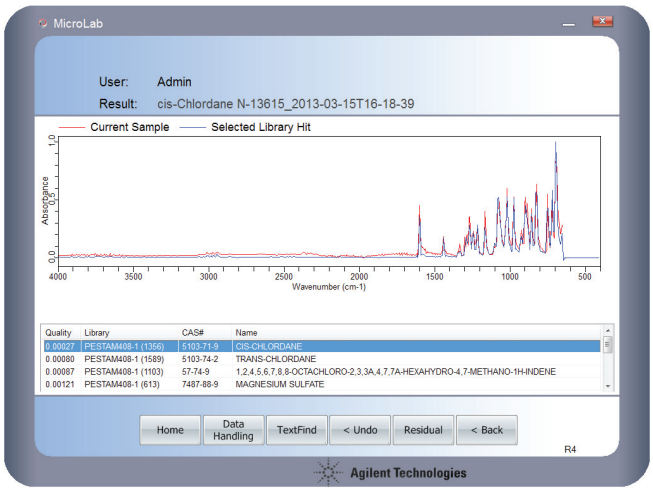


Figure 2. Identification of cis-Chlordane.

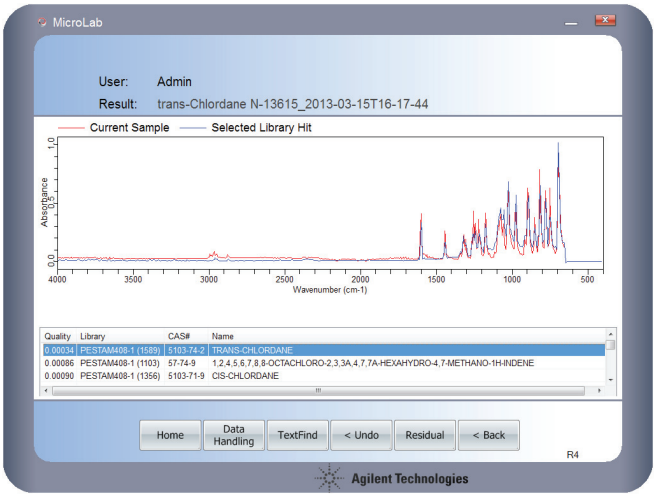


Figure 3. Identification of trans-Chlordane.

Campheclor, a highly toxic and carcinogenic substance that was banned by the Stockholm Convention, is a complex mixture of 200 different compounds formed by the chlorination of camphene. Despite the complexity of the formulation, the IR spectra was easily searched and the identity of the material was ascertained (Figure 4)

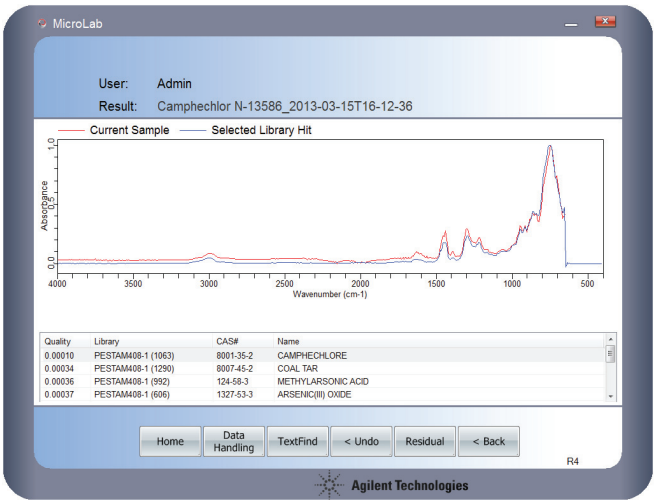


Figure 4. Identification of Campheclor.

Excellent matches were also obtained for lindane and aldrin, potent organochlorine insecticides also banned by the Stockholm Convention (Figures 5,6)

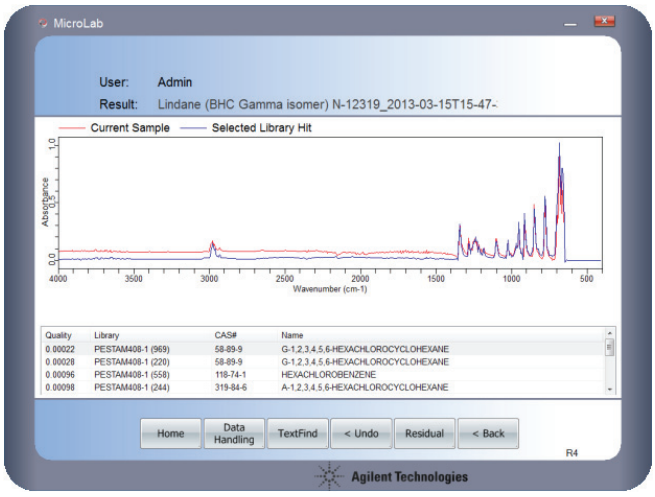


Figure 5. Identification of Lindane.

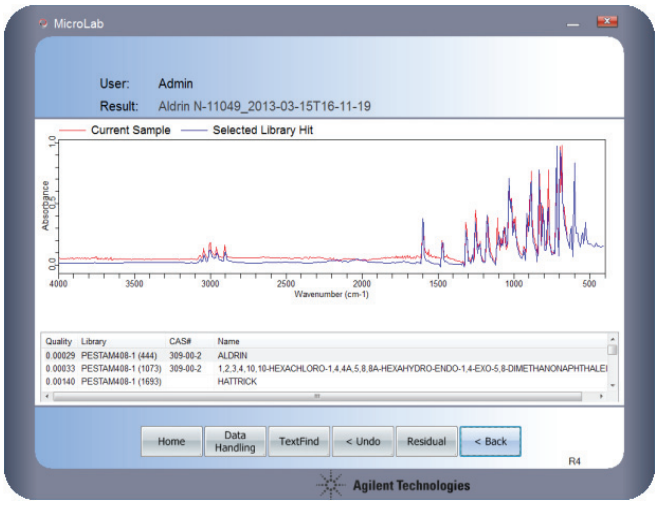


Figure 6. Identification of Aldrin.

Conclusion

FTIR spectroscopy can quickly and easily identify undiluted pesticides with a minimum of sample preparation. The combination of commercially available pesticide data bases combined with the performance and mobility of the Agilent 4500 and 5500 Series FTIR, enable rapid, on-site analysis of suspect product. Adulterated, contaminated or otherwise out-of-specification pesticides can now be analyzed in locations where they are manufactured, shipped, received, stored and sold. Once pesticides are diluted for application to crops, the FTIR analyzers are capable of identification if the active ingredient level is > 5%. For more dilute solutions, or for determining the level of residual pesticide in crops, other technologies are employed[2].

This technology offers port and border control officers the capability to spot check containers for content authenticity. This ensures that pesticide identity is verified prior to application in fields and farms and mitigates the risk of detrimental effects on health, produce, crops and the environment.

Suggested Configuration

0021-010 4500a FTIR Single Reflection ATR

G8046AA#117 ATR Pesticides Library from ST Japan

References

[1] Frederick Fishel, The Global Increase in Counterfeit Pesticides, Institute of Food and Agricultural Sciences, University of Florida (2009).

[2] Agilent Publication, Accelerated Analysis of On-Site Pesticide Detection in Vegetables by Agilent 5975T LTM GC/MSD and TSP, 5990-8067EN, June 8, 2011.

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