Application Note Handheld Chemical Identification



Analysis of Pesticides in the Field using a Handheld Raman Analyzer with SORS

Through-barrier identification of agrochemicals using the Agilent Resolve handheld Raman analyzer



Abstract

The Agilent Resolve Raman handheld through-barrier identification (ID) system is a versatile analyzer that can be deployed on location to identify a broad range of materials, including fertilizers, insecticides, and herbicides. Resolve uses Spatially Offset Raman Spectroscopy (SORS) to identify materials concealed behind barriers such as colored and opaque plastics, dark glass, paper, and fabric.

This application note details how the Resolve Raman system can easily identify specific agrochemical materials in two real-life settings. The first scenario describes the use of the Resolve to certify the identity of pesticides in the field before they were applied to crops. The second example outlines the use of Resolve by customs officials to identify legitimate, illegal, adulterated, or contraband pesticides.

Authors

Ricardo Nobara, Luciana Terra, and Ana Blanco Agilent Technologies, Inc.

Introduction

Pesticide consumption worldwide grew to 4 million metric tons in 2022.¹ This upward trend is expected to continue as the market value is forecast to rise from USD 66.04 billion in 2023 to USD 80.35 billion by 2028.² The pesticide sector includes herbicides, insecticides, fungicides, and other substances that are used to control other types of pests.

Pesticides are heavily regulated, but almost half of all approved products contain active ingredients that have adverse effects on human health.³ These materials, when not controlled correctly, can therefore cause serious health and environmental issues. Also, a significant number of agrochemicals that are banned in the EU and US have been recorded in agrizones such as Latin America. Illegal trade in pesticides⁴, which includes non-registered products, counterfeit, adulterated, repackaged, contraband, or stolen goods, is of concern in some agribusiness zones, and between some countries. This illicit trade is driven by problems faced by farmers, such as delays in registration, differences in taxes on agrochemicals between neighboring countries, shortages, and bans on widely used products.

The Agilent Resolve handheld Raman analyzer is a powerful tool that can be used to identify materials commonly found in agricultural settings (Figure 1). It uses Agilent proprietary **Spatially Offset Raman Spectroscopy (SORS)** technology to identify materials concealed behind barriers such as colored and opaque plastics, dark glass, paper, and fabric. The configuration of the SORS optics also means that Resolve produces high-quality data and reliable results for materials on site, avoiding the costs associated with laboratory testing. As the Resolve is battery-operated, it can be deployed directly in the field to confirm the identity of agricultural materials, such as fertilizers, insecticides, and herbicides, before use on crops. It can also be used by law enforcement to detect adulterated or controlled materials during road checks of materials in transit.



Figure 1. Agilent Resolve handheld Raman analyzer equipped with the "Toxic and Hazardous" spectral library for the quick ID of agricultural chemicals.

Resolve identifies materials through comparison of spectra contained in comprehensive onboard libraries which are available in three packages: Standard, Toxic and Hazardous, and Comprehensive. The Toxic and Hazardous library was used in the "pesticide analysis in customs" part of this study, as it includes a wide selection of fertilizers, herbicides, pesticides, fungicides, and other related agrochemical materials. Also, for any materials of interest not included in the Agilent library, it is possible to build a custom library. New library items can be created using the user library functionality on the Resolve, or using the PC-based Agilent Command Fleet Management Software. The Command management module provides more flexibility than using the Resolve software, with the ability to average measurements, perform small corrections, and add metadata. Once a library has been created, a Command library file can be generated for uploading from the PC onto the Resolve or onto multiple (a fleet of) Resolve analyzers.

The library creation process in Command is fast and simple, and allows the user to create a targeted detection capability, as undertaken in the "pesticide analysis before fumigation" part of this study.



Figure 2. Screenshot of Agilent Command Fleet Management Software – PC-based management module software that enables the addition of spectra to a user-created library for the Agilent Resolve handheld Raman analyzer.

Pesticide analysis before fumigation

Resolve was deployed in South America to certify the ID of pesticides in the field before they were applied to crops. The portability of Resolve, together with the flexibility to create targeted libraries, makes the Resolve a powerful tool for use in rural locations. Other benefits of the analyzer include:

- Resolve could be easily deployed in the field or at the location where agrochemical materials are kept, avoiding the time and costs associated with analyzing samples in a laboratory.
- Materials were measured through the native container or in a vial, without the need for sample preparation.
- No consumables were required for the analysis; just point-and-shoot the handheld analyzer.
- Fast analysis times were achieved, with ID generated within two minutes.
- High quality data was obtained for all scans.
- Flexibility to create custom libraries that related to locally used materials.

To obtain the best quality data to add to a custom Command library for pesticides for Resolve, the nine pesticide samples summarized in Table 1 were measured in their native containers and in glass vials. Figure 3 shows a Raman spectrum for each of the nine pesticides and the analysis of one of the pesticide samples (triclopyr) through its native container. The spectra were matched against the newly created User/Command library for pesticides and the identity of "TROP" (triclopyr) was verified before it was sprayed on the crops.

Table 1. Items measured by the Agilent Resolveto add to the custom Command spectral libraryand commercial use of materials.

Item	Use
Proclaim	Insecticide
Chlorpyrifos	Insecticide
Abamectin	Insecticide
Glyphosate	Herbicide
Triclon Triclopyr	Herbicide
Chlorimuron-ethyl	Herbicide
Metsulfuron-methyl	Herbicide
Tebuconazole	Fungicide
Picoxystrobin	Fungicide



Figure 3. Agilent Resolve Raman SORS spectra of all pesticides analyzed during the field operation, separated into three categories by commercial use: insecticides (A), herbicides (B), and fungicides (C). Analysis of one of the pesticide samples through its native container (D), match to User/Command library for "TROP" (triclopyr) (E), and delivery of pesticide to crops after verification with Resolve (F).

Pesticide analysis in customs

Control of pesticides and other agrochemicals moving across international borders is key to managing the risks to the environment and human health posed by banned or adulterated products.

A South American international border customs organization used the Resolve analyzer to verify the contents of several shipments of agricultural materials. Benefits of the method included:

- The SORS through-barrier measurement capability of the Resolve made the confirmatory task of pesticide ID more efficient, as there was no need for sample preparation.
- Samples contained in different types of barriers could be investigated – plastic containers, paper sacks, etc.

- No consumables were required.
- Fast analysis times were achieved, with ID generated within two minutes.
- High-quality matches to the Agilent on-board Toxic and Hazardous spectral library.
- Confirmation of the shipment of materials.

Several different consignments with varying container types were analyzed using Resolve SORS through-barrier capability, as shown in Figure 4. During the investigation, two pesticide shipments were confirmed, the herbicide diflufenican and the insecticide diflubenzuron. Resolve SORS spectra for the two compounds are shown in Figure 5. Both compounds matched to the respective on-board library items with a match quality of 97%. Figure 5 shows the on-screen result for diflufenican.



Figure 4. Operators analyze different consignments of agrochemicals using the Agilent Resolve handheld Raman analyzer



Figure 5. (A) The Agilent Resolve analyzer match to the Agilent library entry for diflufenican, confirming the ID stated on the documentation. The product was analyzed through its native paper sack on location at the customs site using the Resolve in SORS through-barrier mode. (B) Agilent Resolve SORS spectra for the two pesticides found during the customs operation.

Conclusion

This application note illustrates how the Agilent Resolve Raman handheld analyzer can be used for pesticide identification in different settings, highlighting the flexibility and capabilities of the instrument. The qualities that make Resolve an excellent choice for on-site pesticide identification include:

- The ability of SORS to measure compounds through containers.
- Ease of identifying compounds against comprehensive on-board spectral libraries.
- Simple creation of new, custom spectral libraries using Resolve or Agilent Command Fleet Management software.
- The portability of the lightweight, battery-powered instrument.

Resolve correctly identified the herbicide, triclopyr, before its application to crops. It was also used by customs officials to verify that the ID of pesticides matched the information on the accompanying paperwork.

References

- Tostado, L., Pesticides and Agriculture: Dangerous Substances, *Heinrich-Böll-Stiftung*, **2022**, accessed Oct 2023, https://eu.boell.org/en/PesticideAtlas-agriculture
- Crop Protection Chemicals Market Size & Share Analysis - Growth Trends & Forecasts (2023–2028), Mordor Intelligence, accessed Oct 2023, https://www. mordorintelligence.com/industry-reports/global-cropprotection-chemicals-pesticides-market-industry
- Lopes-Ferreira, M.; Maleski, A. L. A.; Balan-Lima, L.; Bernardo, J. T. G.; Hipolito, L. M.; Seni-Silva, A.C.; Batista-Filho, J.; Falcao, M. A. P.; Lima, C. Impact of Pesticides on Human Health in the Last Six Years in Brazil. *Int. J. Environ. Res. Public Health*, **2022**, *19(6)*, 3198. doi: 10.3390/ijerph19063198. PMID: 35328887; PMCID: PMC8951416.
- 4. Crop Life Latin America, What are the Forms of Illegal Trade in Agricultural Inputs in Latin America?, 2021, accessed Oct 2023, https://www.croplifela.org/en/ whats-new/news/what-are-the-forms-of-illegal-trade-inagricultural-inputs-in-latin-america
- https://news.mongabay.com/2023/05/borders-betweenmercosur-countries-have-become-a-hub-for-traffickingagrochemicals/#:~:text=From%20June%20to%20 September%202022,were%20valued%20at%20about%20 %24830%2C000.

Further information

- Resolve Handheld Raman Analyzer
- Command Fleet Management Software
- Resolve Handheld Raman Analyzer FAQs
- Raman Spectroscopy FAQs

www.agilent.com

DE85822759

This information is subject to change without notice.

© Agilent Technologies, Inc. 2023 Printed in the USA, November 16, 2023 5994-6936EN

