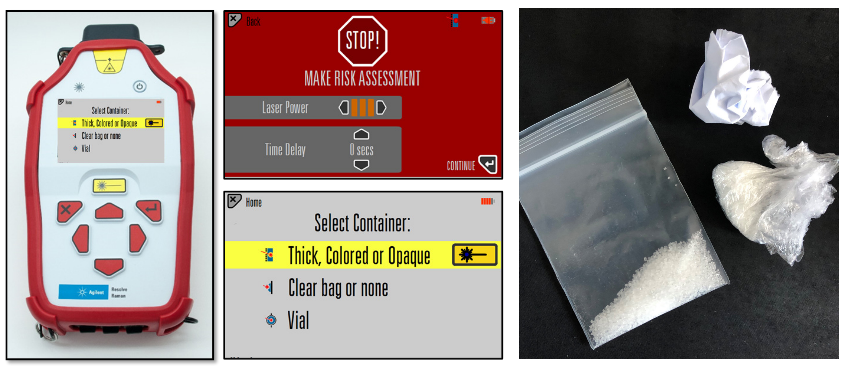
Application Note

Handheld Chemical Identification

Direct Identification of Packaged Substances using the Agilent Resolve Handheld Raman Analyzer

Comparison of conventional Raman and SORS through-barrier mode in plastic wrapping



Author

Leung Tang
Agilent Technologies, Inc.

Abstract

The Agilent Resolve handheld Raman analyzer uses conventional Raman and spatially offset Raman spectroscopy (SORS) through-barrier Raman techniques to probe the contents of wrapped or contained materials. No sample preparation is required, enabling the remote, on-site, or at-site analysis of samples.

This study compared the depth of penetration of conventional and through-barrier modes of the Resolve analyzer for the identification of white sugar (used to represent a controlled substance) through packaging material. Operating in the conventional surface mode, the Resolve analyzer correctly identified the relatively weak scattering of sugar behind multiple layers of low-density polyethylene (LDPE) bags. The thickness of the wrapping was approximately 460 µm and the analysis time was less than 1 minute. Using the Resolve in SORS through-barrier mode provided the correct answer through 67 layers of LDPE. The thickness of the wrapping was approximately 2.7 mm and the analysis time was less than 2 minutes.

The results show the ability of the Resolve analyzer to identify compounds through layers of plastic, which makes it a valuable tool for law enforcement in detecting concealed drugs and illicit substances.

Introduction

Raman spectrometers probe materials using monochromatic laser light, usually at visible or near-infrared (NIR) wavelengths. When a sample is illuminated, most of the light is scattered without a change in energy—this is termed Rayleigh scattering. However, a small proportion of photons is scattered, resulting in a loss or gain of energy due to molecular vibrations—this phenomenon is termed the Raman effect or Raman scattering. The energies of these vibrations are specific to the composition and structure of the molecules in a sample, which is why Raman is referred to as a chemical fingerprint technique.

Conventional Raman spectroscopy involves illuminating a sample with a laser followed by the detection of the scattered light, whereas SORS through-barrier mode uses multiple measurements to probe the subsurface of a sample. SORS often allows materials to be identified inside thick, sealed, colored, and opaque containers, which is not achievable using conventional surface-mode Raman. Typically, conventional Raman can see through up to a few hundred microns (µm) of low-scatter barrier material while SORS can detect samples through thicker barriers. However, one study evaluated the effectiveness of both techniques for the identification of ethanol through 1 mm layers of polyethylene terephthalate (PET), a low-haze (clear) plastic. Spectra were collected through 9 mm of PET using conventional Raman and 21 mm of PET using SORS through-barrier mode.[1]

Controlled substances are often packaged in consumer zip lock bags, which are often made from polyethylene and have a thickness ranging from approximately 50 to 200 µm. LDPE is the preferred polymer for making zip lock bags because its lower crystallinity provides the bags with improved tear resistance compared to high density polyethylene (HDPE).[2]

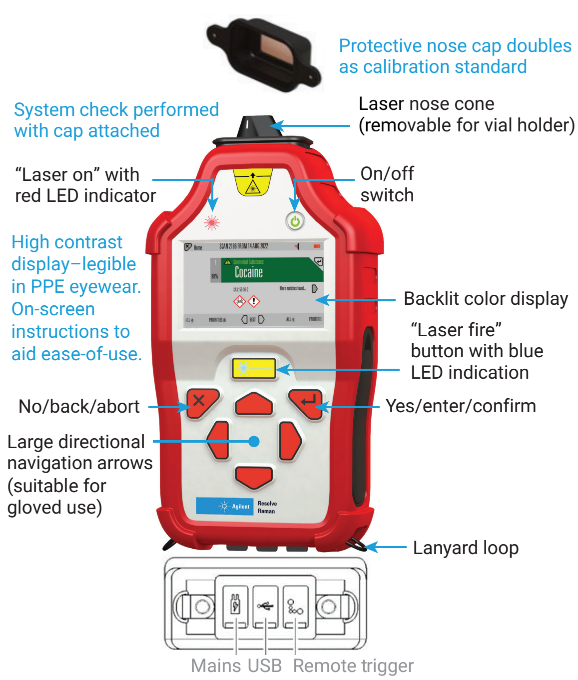
To test the capabilities of the conventional Raman mode and SORS mode using the Agilent Resolve handheld Raman analyzer, white granulated sugar was detected in LDPE zip lock bags. Sugar in the form of crystallized sucrose was used as a surrogate white powder (representing a controlled substance) since it is a relatively weak Raman scatterer. As controlled substances are often padded with layers of plastic, the primary bag of sugar was inserted inside other LDPE bags, or multiple LDPE bags were placed on top of the primary bag before analysis.

Experimental

Instrumentation

The Resolve handheld Raman analyzer is a flexible spectrometer that is widely used for the identification of chemicals, including controlled substances and hazardous materials. Details of the instrument and its key attributes are outlined in Figure 1.

In this study, the Resolve analyzer was used to identify samples in surface and SORS through-barrier modes. The mode of analysis is selected in the Agilent Raman Resolve software, as shown in Figure 2. Conventional mode is often referred to as a "surface scan" and appears in the Raman Resolve software as "Glass, Clear Bag or None". SORS scan mode is often referred to



Key attributes

- Choice of modes
  - Surface (conventional)
  - SORS (through barrier)
  - Vial
  - Stand off (non-contact)
- Low power consumption
- Built-in libraries
  - Updated regularly
- User custom library options
  - Easy addition of spectra
  - Shock-resistant and IP67
- 830 nm Class 3B laser
- Auto-scheduled system checks
- On-screen guidance
- Reachback contact service to Agilent for queries

Figure 1. Overview of the Agilent Resolve handheld Raman analyzer.

as "through-barrier" and appears in the software as the "Thick, Colored or Opaque". Figure 2 shows that the SORS method fires the laser twice sequentially, once orthogonally (1) and once at an offset angle (2), whereas the conventional method relies on the orthogonal emission only.

Samples

Prepacked granulated white sugar was obtained in paper sachets (Figure 3C). The sugar was decanted into a single LDPE zip bag, into plastic wrap (cellophane), and analyzed as received in its paper wrapper, as shown in Figures 3A to 3C. The packaging was chosen to reflect the three most common wrappers used for street drugs.

LDPE zip bags

A digital micrometer with 0.001 mm graduation and clutched gearing was used for the cumulative and individual layer thickness measurements of the LDPE bags.

For the bag-inside-bag experiment, the primary small LDPE sample bag containing the sugar was 7 × 5 cm and 40 µm thick (Figure 3A). The longer LDPE bags were 18 × 7 cm and varied in thickness from 25, 30, and 40 µm.

For the layered experiment, the primary small LDPE bag was 7 × 5 cm with a thickness of 60 µm per layer and contained approximately 7.5 g of sugar (three paper sachets of sugar). The bag of sugar was secured to a small clipboard between two blue 4.7 mm deep shims, as shown in Figure 4. The main advantage of this setup was to facilitate the addition and measurement of multiple LDPE bag layers and ease of adding or removing layers. The overlaid LDPE bags were 25 × 5 cm with a single layer thickness of 40 µm, totaling a combined layer thickness of 80 µm per bag.

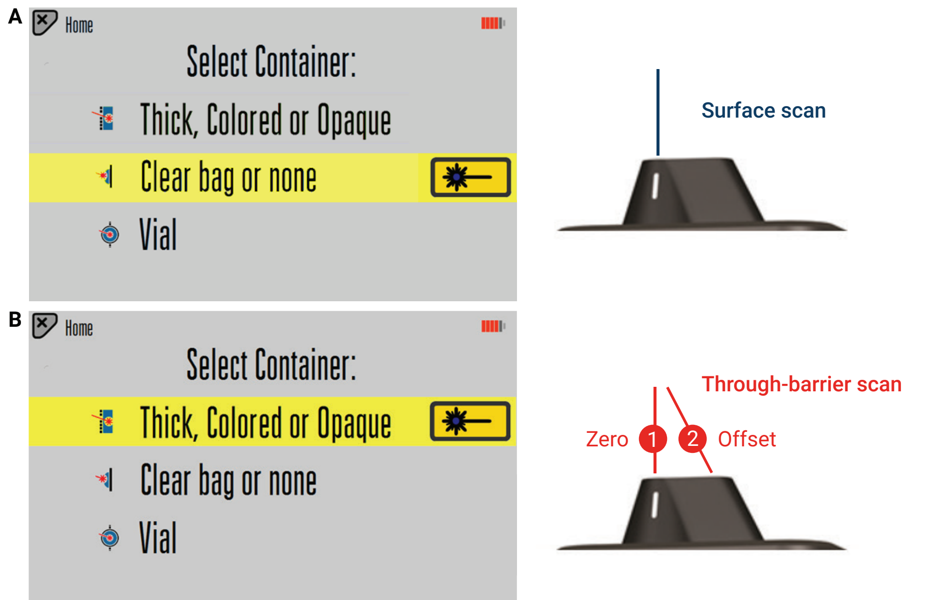


Figure 2. (A) Agilent Raman Resolve software screen (left) showing how to conduct a surface scan (right) by selecting "Clear bag or none" mode. (B) Agilent Raman Resolve software screen (left) showing how to conduct a SORS/through-barrier scan by selecting "Thick, Colored or Opaque" mode. The 830 nm laser is a nonvisible NIR laser, so the blue and red colors are used for illustration purposes only.

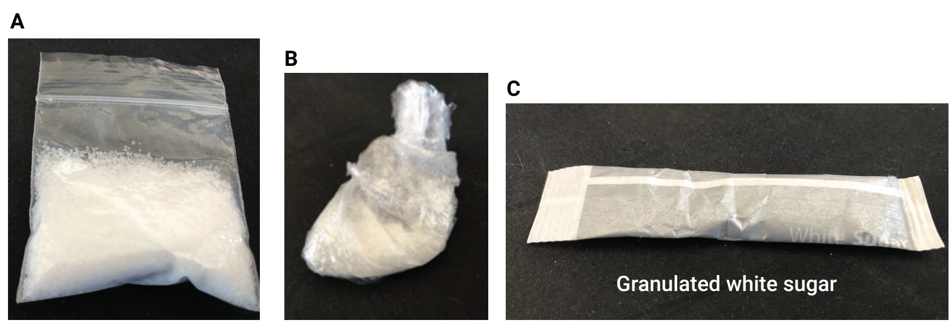


Figure 3. Examples of the packaged sugar samples tested in this study.

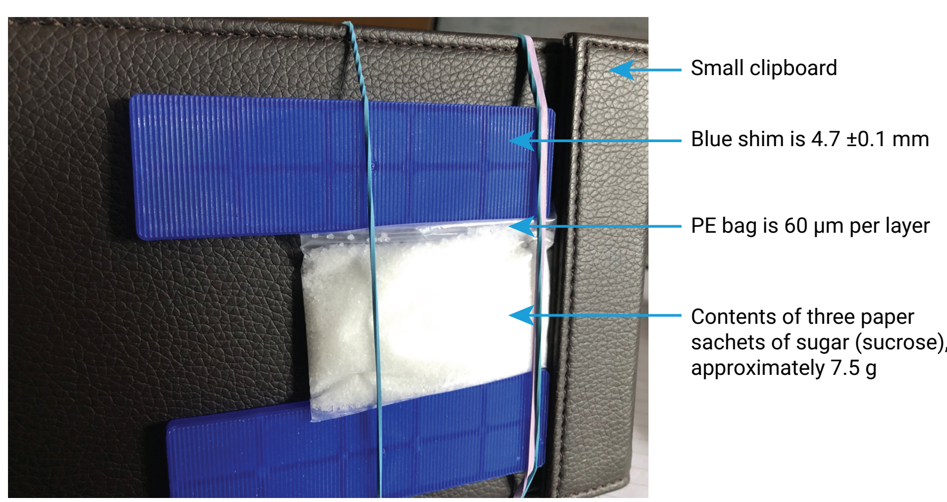


Figure 4. The sample setup for the primary PE LDPE bag containing sugar from three paper sachets.

Results and discussion

Initial testing of sugar samples

The three packaged sugar samples (Figure 3) were analyzed using the Resolve handheld Raman analyzer in both surface and through-barrier modes. The system identifies materials by comparing the acquired spectra with reference spectra of known compounds in the system's comprehensive spectral libraries. The results are shown in Table 1.

Sucrose or sugar (which are chemically identical) was correctly identified through the LDPE bag and plastic wrap in both modes. However, the opaque paper wrapper of sample C contributed to the Raman spectra in surface mode, leading to a reported result of 93.5% sugar and cellulose. The thickness of the paper layer was measured using a digital micrometer and was found to be 130 µm. The sample in the paper sachet was correctly identified with a 98% match to sucrose using the SORS through-barrier mode, demonstrating the effectiveness of the technique for the testing of samples in opaque packets.

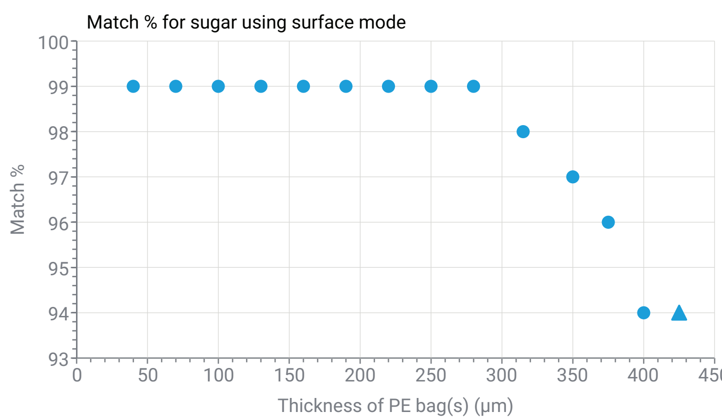
Effects of multiple layers of LDPE on conventional surface scan mode

Sugar was placed into a small sized LDPE bag and measured by the Resolve analyzer in surface scan mode. The small bag of sugar was then put into another LPDE bag and the contents were rescanned using the analyzer. This process was repeated until the material identification match produced an inaccurate result.

The results obtained from the study are presented in both graphical and tabular formats in Figure 5. The match % for sugar (sucrose) for one to nine layers of LDPE was 99%. Each additional layer of LDPE above a thickness of 300 µm led to a drop in the match % to sucrose. At 425 µm thickness, the match was no longer reported as a single compound. The data highlight the capabilities of conventional Raman, which correctly identified sugar through the first 13 layers of LDPE.

Table 1. Results of the identification of sugar (sucrose) samples and the match % using the Agilent Resolve handheld Raman analyzer in both conventional surface scan mode and SORS through-barrier mode.

Sample	Material Identification	
	Surface Mode	Through-Barrier Mode
A. Sugar in LDPE lock bag	100% Sugar	100% Sucrose
B. Sugar in cellophane (plastic wrap)	100% Sucrose	100% Sucrose
C. Sugar in a paper sachet	93.5% Sugar and cellulose	98% Sucrose



Thickness (µm)	Match %
40	99% Sugar
70	99% Sugar
100	99% Sugar
130	99% Sugar
160	99% Sugar
190	99% Sugar
220	99% Sugar
250	99% Sugar
280	99% Sugar
315	98% Sugar
350	97% Sugar
375	96% Sugar
400	94% Sugar
425 ▲	94% Sugar + other

Figure 5. Agilent Resolve handheld Raman analyzer in surface scan mode % match results for sugar in a small LDPE bag (one layer). The bag of sugar was systematically inserted into more LDPE bags (up to 14 layers and a cumulative thickness of 424 µm). The thickness of the bags was 25, 30, 35, or 40 µm.

Effects of layering LDPE bags on surface and through-barrier modes

The use of multiple layers of LDPE zip lock bags as a proxy for the determination of the thickness capability of the Resolve analyzer in surface and through-barrier modes represents a worst-case scenario. The small air gap between each layer makes detection of the sample more difficult compared to the equivalent thickness of unlayered (moulded) LDPE. The thickness limit of solid LDPE would be significantly higher.

LDPE is a branched form of polyethylene that remains flexible due to the presence of short and long branches.[3] All plastics have a degree of haze, which affects the clarity of the material. LDPE has a wide haze range from 1.3 to 27%[4] (haze can be engineered to suit the end use of the plastic). The effect of haze is shown in Figures 6A to 6H. Each additional PE bag has a bilayer thickness of 80 µm.

Conventional surface mode

To determine the laser penetration depth of layered (plied) PE bags, LDPE bags were added successively on top of the primary bag of sugar. This layering was repeated until the Resolve analyzer operating in surface mode reported results for the barrier material rather than for the sugar sample. To test the effects of the thickness of LDPE, the laser nose cone of the Resolve analyzer (Figure 1) was pushed against the sample and barrier bags to minimize the air gap between the layers. In active use, the Resolve can be applied firmly against the packaged sample.

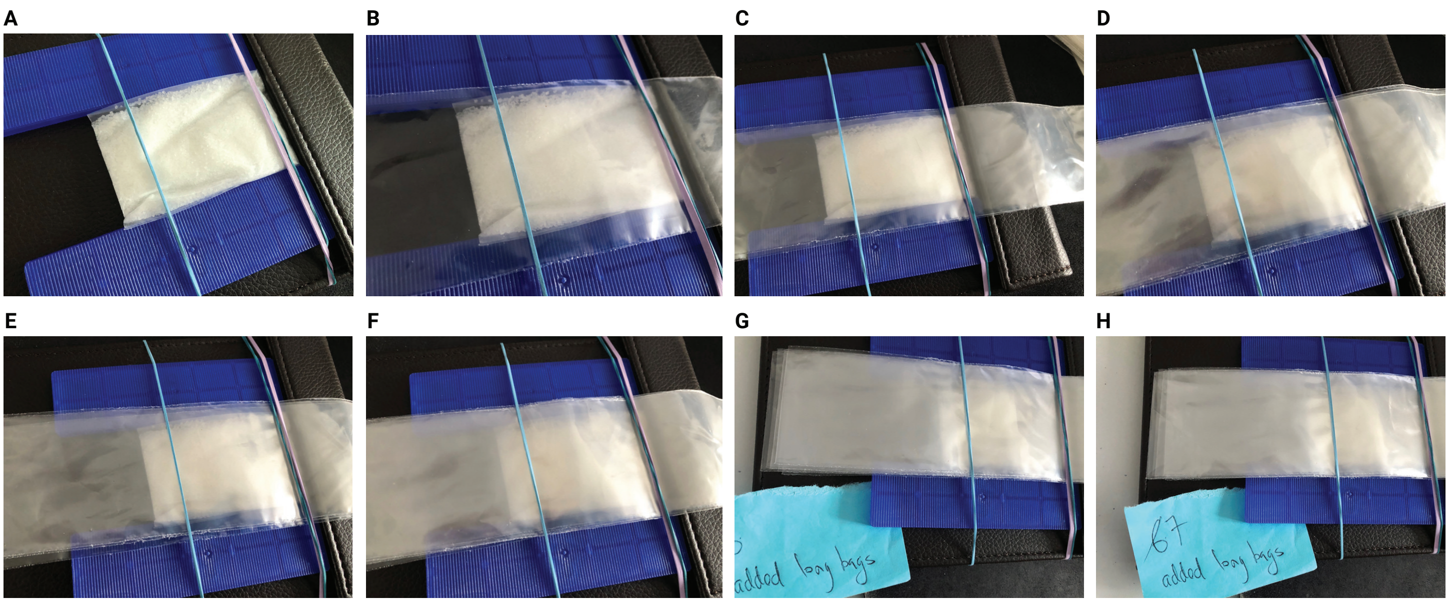


Figure 6. (A) Sugar in PE bag (60 µm single layer or ply), (B) = A + 1 PE bag (140 µm – 3 layers), (C) = A + 2 PE bags (220 µm), (D) = A + 3 PE bags (300 µm), (E) = A + 4 PE bags (380 µm), (F) = A + 5 PE bags (460 µm), (G) = A + 6 PE bags (540 µm), and (H) = A + 7 PE bags (620 µm – 15 layers or plies).

Sucrose/sugar was correctly identified by the Resolve analyzer in surface mode for up to 11 layers (460 µm ply thickness) of LDPE, as shown in Table 2 and Figure 7. The results show that the penetration of the laser through the layers of LDPE is impeded by the barrier when more layers of LDPE are added. The first change in the library match result from sucrose or powdered sugar to sugar and other components was observed for 13 and 15 plies (540 and 620 µm respectively) of LDPE results. This transition suggests that the PE barrier material was contributing to the Raman spectra. As the plies increased, the laser illuminated less of the sugar and more of the PE. The results from 17 to 31 plies (700 to 1,260 µm) of LDPE report beeswax/stearic acid/polyethylene as the primary component and sucrose as the secondary component. Finally, for the conventional surface mode, plies from 33 to 51 (1,340 to 2,060 µm) were identified as a single compound match that related purely to the PE bags.

Table 2. Agilent Resolve handheld Raman analyzer in conventional surface mode for the identification of sugar, showing layer thickness (µm) and primary % match results. Each subsequent result after the primary 60 µm LDPE bag containing 4.7 mm of sugar adds two layers totaling 80 µm for each additional PE bag.

Thickness (µm)	%Match
60	99% Sucrose
140	99% Sucrose
220	99% Sucrose
300	98% Sucrose
380	97% Powdered sugar
460	96% Powdered sugar
540	94% Sugar + other
620	95% Sugar + other
700	95% Beeswax + Sucrose
780	94% Stearic acid + sucrose
860	94% Stearic acid + sucrose
940	94% Stearic acid + sucrose
1,020	93% Stearic acid + sucrose
1,100	94% Beeswax, refined yellow + sucrose

Thickness (µm)	%Match
1,180	95% Polyethylene + sucrose
1,260	95% [Plastic] polyethylene-co-propylene + sucrose
1,340	94% Candelilla wax
1,420	96% [Plastic] polyethylene
1,500	97% [Plastic] polyethylene
1,580	97% [Plastic] polyethylene
1,660	98% [Plastic] polyethylene
1,740	98% [Plastic] polyethylene
1,820	98% [Plastic] polyethylene
1,900	98% [Plastic] polyethylene
1,980	97% [Plastic] polyethylene
2,060	98% [Plastic] polyethylene

(green)	Sucrose (sugar)
(yellow)	Sugar and other
(orange)	Other and sucrose
(brown)	Barrier-related

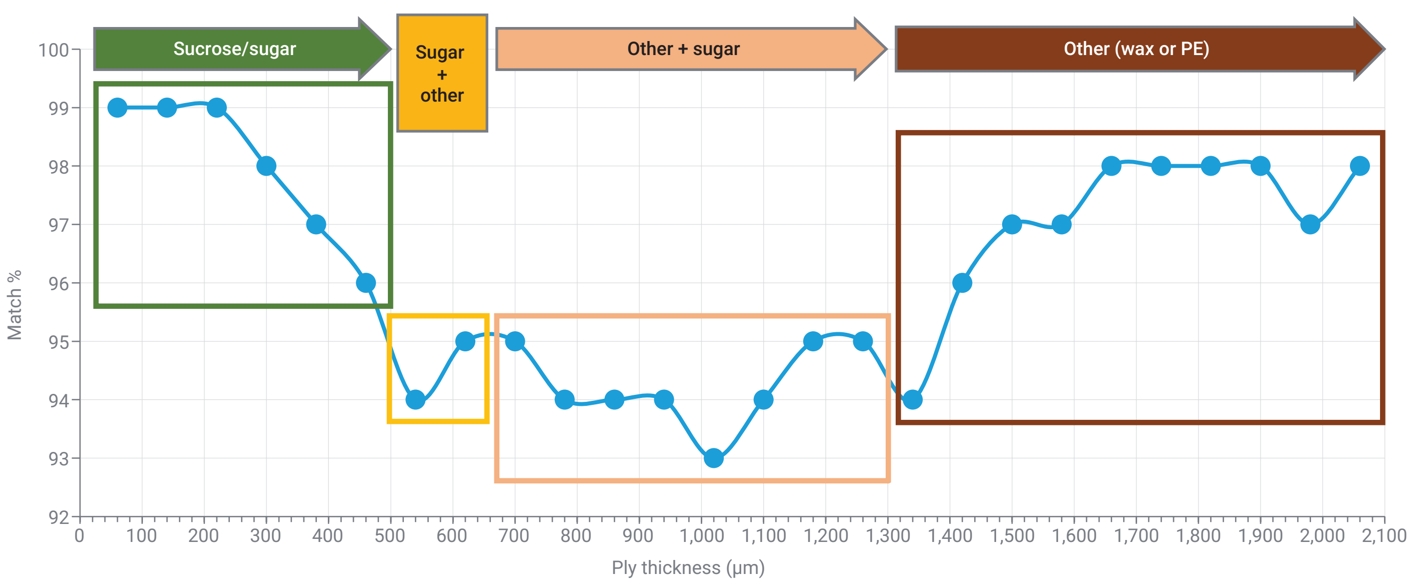


Figure 7. Agilent Resolve handheld Raman analyzer conventional surface mode results for LDPE bags stacked on top of the primary LDPE bag containing sugar (crystallized granulated sucrose) with increasing ply thickness.

SORS through-barrier mode

The same protocol was followed to gather data using the Resolve handheld Raman analyzer in the SORS through-barrier mode. The graph in Figure 8 shows that the limit of correct identification of sugar as a single component extended to 2.7 mm of plied PE bags (compared to 0.46 mm or 460 µm in surface mode). The results show that the SORS through-barrier measurement mode can correctly identify samples packaged in LDPE with up to six times the layer limit thickness of conventional mode.

Using SORS through-barrier mode, the Resolve analyzer correctly identified sugar behind 2.7 mm (69 plies) of LDPE, although a small match % dip occurred at 460 µm. This thickness coincides with the limit of conventional surface mode and the first transition in the results in that mode (Figure 7). Beyond 2.7 mm, the library match was to stearic acid or wax.

Other barrier materials

The thickness limit observed in these tests is not representative of all types of plastic or barrier materials. The barrier selected in this study shows added difficulties due to the multiple layers, when compared to a single, or few layered plastic of the same thickness. At 67 plies/layers of LDPE, the polymer appears opaque and has a near white appearance. When laser light is shone through a laminate, each layer-to-layer interface will scatter a small amount of light. Also, while the bags are nominally clear individually, in a layered pile there will be greater haze, which also attenuates the laser's ability to interact with the sugar contents (Figure 6). In a similar experiment using SORS, ethanol (in a vial) was correctly identified through clear 1 mm PET sheets, up to a total thickness of 21 mm.[1]

In a separate study, the Resolve analyzer SORS through-barrier mode successfully identified the compounds of 42 samples that were either seized or surrendered at a large social gathering.[5] The samples included ketamine, cocaine, MDMA, and caffeine. The Resolve analyzer also successfully identified cocaine in a zip lock bag that was wrapped in multiple layers of transparent sticky tape, plastic wrapping, and paper. The use of tape as a means of concealment and scent avoidance is a common practice for individuals trying to hide the presence of drugs such as cocaine from detection. SORS is an effective technique for the detection of cocaine (and other controlled substances) through various layers of material.

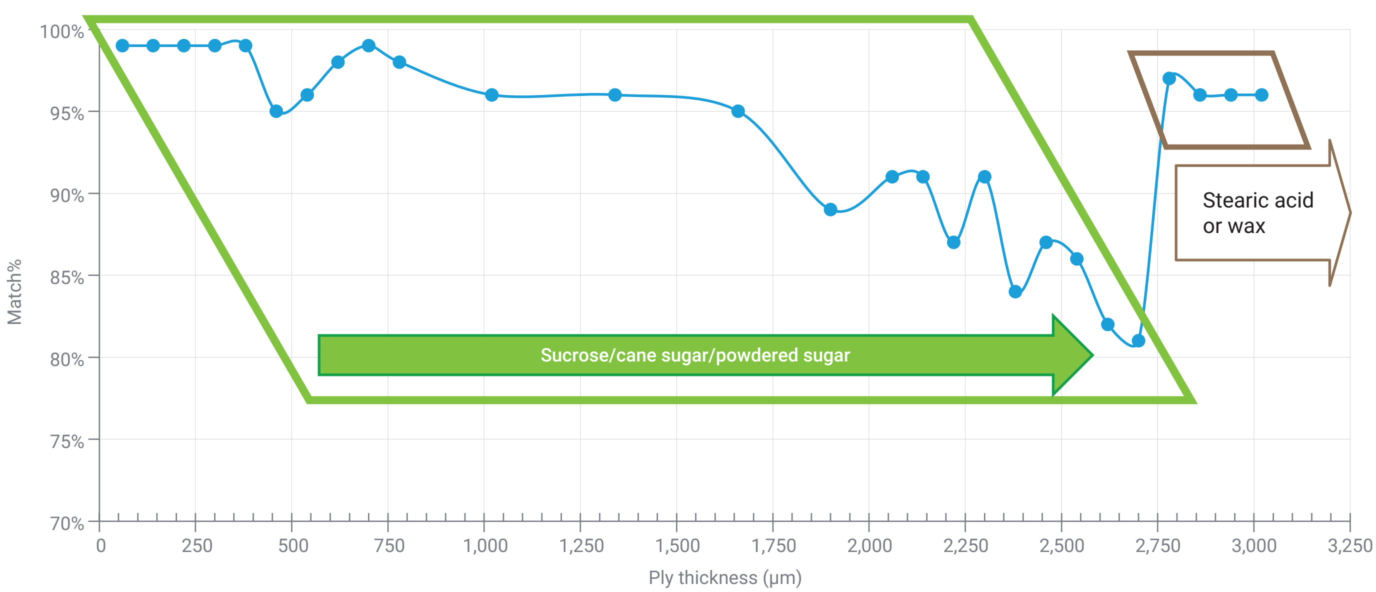


Figure 8. SORS through barrier match % results for sugar in the primary LDPE bag that was overlaid with other LDPE bags. All the correctly identified sample results (sucrose/cane sugar/powdered sugar) are highlighted in the green area.

Conclusion

The Agilent Resolve handheld Raman analyzer identified sugar (sucrose) contained in a low-density polyethylene (LDPE) zip lock bag and plastic film wrap using traditional Raman (surface) and spatially offset Raman spectroscopy (SORS) through-barrier Raman techniques. However, SORS mode was more effective for the determination of sugar in an opaque, paper wrapper than surface mode.

The depth penetration tests of both modes of analysis using multiple layers of LDPE bags also highlighted the benefits of the SORS technique for the analysis of substances wrapped or contained in multiple layers of plastic. In SORS through-barrier mode, the Resolve analyzer identified sugar behind 2.7 mm of LDPE, equivalent to 67 more layers of LDPE than using surface mode.

Also, all polymers have some degree of haze that can impact the sensitivity of conventional Raman spectroscopy in surface mode. While the haze of LDPE ranges from ~1 to 25%, the SORS results reported in this study compared well with published data that investigated ethanol behind sheets of polyethylene terephthalate (PET), a low-haze polymer.

The Resolve analyzer SORS through-barrier mode provides accurate results within 2 minutes through single to multiple layers of plastic and opaque materials. The method allows nondestructive and rapid identification of compounds and substances, making it useful in various applications, including screenings for drugs hidden in opaque containers and vessels.

References

1. Nicolson, F. *et al.* Through Barrier Detection of Ethanol Using Handheld Raman Spectroscopy—Conventional Raman Versus Spatially Offset Raman Spectroscopy (SORS), *J. Raman Spectrosc.* **2017**, *48*, *12*, 1828–1838. https://doi.org/10.1002/jrs.5258
2. Jordan, J. L. *et al.* Mechanical Properties of Low Density Polyethylene, *J. Dynamic Behavior Mater*. **2016**, *2*, 411–420. https://doi.org/10.1007/s40870-016-0076-0
3. Poh, L. *et al.* Characterization of Industrial Low-Density Polyethylene: a Thermal, Dynamic Mechanical, and Rheological Investigation. *Rheol. Acta* **2022**, *61*, 701–720. https://doi.org/10.1007/s00397-022-01360-1
4. Definition of Haze - Optical Property, Omnexus, accessed August **2023**. https://omnexus.specialchem.com/polymer-properties/properties/haze
5. Tang, L. Direct Identification of Street Drugs Using an Agilent Resolve Handheld Raman Analyzer, *Agilent Technologies application note*, publication number 5994-6693EN, **2023**.

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Printed in the USA, September 6, 2023
5994-6690EN

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