Application Note

Handheld Chemical Identification

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Detection of Endangered Species Using the Agilent Resolve Raman Analyzer

Improving the detection range of the handheld Raman analyzer using SORS

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Abstract

The Agilent Resolve handheld Raman system is a versatile analyzer that can be deployed on location to identify a broad range of materials. It uses traditional surface analysis mode and through-barrier mode through Agilent's proprietary spatially offset Raman spectroscopy (SORS) technology. SORS enables samples that are concealed behind barriers such as colored and opaque plastics, paper, and highly pigmented paints and varnishes to be identified. This application note details how the Resolve Raman system can be used to detect concealed endangered species products using SORS. Data are presented that show the effectiveness of Resolve operating in traditional surface mode to distinguish ivory from a plastic substitute. Further analysis of endangered animal products using surface mode enabled the division of animal products into two broad categories: mineral-based and protein-based. Principal components analysis (PCA) was used to further differentiate the protein-based samples, which included pangolin scale, rhino horn, dried seahorse, and totoaba fish bladder, based on their spectral differences.

Introduction

The high value of wildlife trafficking, estimated at between 7.8 and 10 billion USD, has attracted the involvement of international criminal networks.[1] As well as being illegal, wildlife trade poses a significant threat to local ecosystems, leading to the depletion of populations of often endangered species, and often inflicts considerable suffering upon the animals involved. The illicit trade is driven by a diverse range of demands, as highlighted by Earth League International. The most well-known examples of traded animal parts include rhino horn, pangolin scale, and totoaba fish bladder for their perceived medicinal properties and ivory for jewelry, ornaments, and accessories.

The Agilent Resolve Handheld Raman Analyzer is a powerful tool that can be used to identify materials commonly found in a border control setting (Figure 1). It uses Agilent proprietary SORS technology to identify materials concealed behind barriers such as colored and opaque plastics, dark glass, paper, and fabric. The Resolve identifies materials through the comparison of spectra contained in comprehensive onboard libraries, which are available in three packages: Standard, Toxic and Hazardous, and Comprehensive. For example, Air Cargo Customs in Hong Kong published their inclusion of Resolve in their tool kit to identify concealed drugs and concealed animal parts.[2] The Standard library was used to investigate the endangered species samples in this study. For any material of interest not included in the Agilent library, it is possible to build a custom library. This can be done using the user library functionality on the Resolve handheld analyzer or through the PC-based Agilent Command Fleet Management Software.

Figure 1. The Agilent Resolve handheld Raman analyzer can detect a range of concealed materials such as narcotics, explosives, chemical warfare agents, and general chemicals.

Ivory detection with Resolve

Raman spectroscopy can be used as an additional tool to help identify ivory, complementing visual inspections (e.g., Schreger lines). Although identification of ivory using Raman is possible, differentiation between bone and ivory using this spectroscopic technique alone is difficult, since both materials share the same chemical composition. The Resolve Standard library includes a reference spectrum of ivory, as shown in Figure 2.

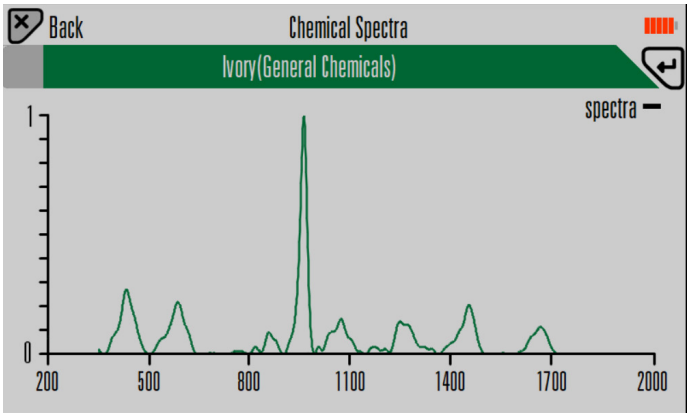

Figure 2. Spectrum of ivory in the Standard library of the Agilent Resolve handheld Raman analyzer.

Illicit traders in ivory often use paint or varnish to alter its appearance and evade detection. The pigments in paint can generate a fluorescent background that obscures the ivory signature, impeding its identification using conventional surface mode Raman. However, this interference can be overcome using SORS technology[3], as used in the through-barrier mode of the Resolve analyzer. SORS reduces the contribution from the surface layer of paint or varnish by acquiring sub-surface chemical information. The method can be used to aid the detection of ivory.

When dealing with convincing ivory substitutes made from plastics or resins, Resolve can easily differentiate between the authentic animal-origin material and synthetic materials. Figure 3 shows that plastic tusks can easily be differentiated from bone and ivory using the Resolve in surface analysis mode.

Benefits of the Resolve for the detection of ivory include:

- The SORS through-barrier measurement technique can help identify ivory concealed behind layers of paint or varnish.
- Resolve can easily differentiate between plastic ivory substitutes and real animal-origin materials.

Identification of other protected endangered species

The illicit trade of endangered species includes many products intended for medicinal, decorative, or cultural purposes. Some common endangered-animal products that were confiscated at various international borders were measured alongside corresponding items provided by a museum. The samples included bone, ivory, teeth, rhino horn, seahorse, totoaba fish bladder, pangolin scale, armadillo scale, and rhino toenail.

Based on the measurements of these natural materials, the nine items analyzed by the Resolve analyzer (Figure 4) were divided into two groups:

- **Group 1:** Mineral-based items including bone, ivory, teeth, and armadillo scale.
- **Group 2:** Protein-based items including seahorse, totoaba fish bladder, rhino toenail, pangolin scale, and rhino horn.

The chemical nature of the mineral (hydroxyapatite) composition of items in group 1 did not vary sufficiently to confidently differentiate between these items using Raman spectroscopy. A second technique would therefore be recommended to confirm the identity of these samples.

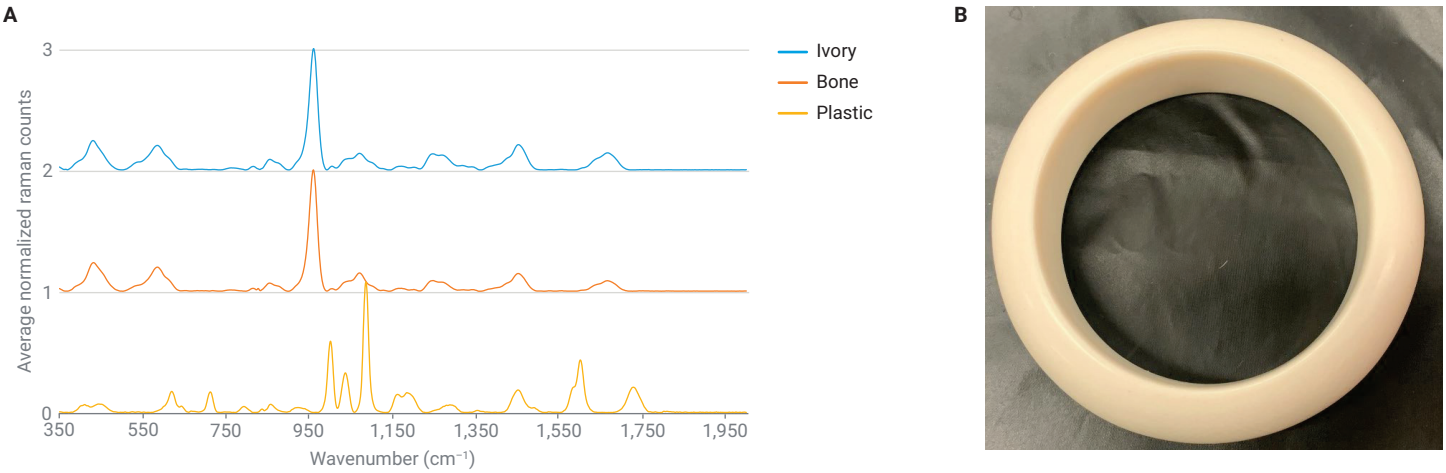

Figure 3. (A) Raman spectra of ivory (blue), bone (orange), and a plastic tusk (yellow) by an Agilent Resolve handheld Raman analyzer. (B) A ring made of ivory.

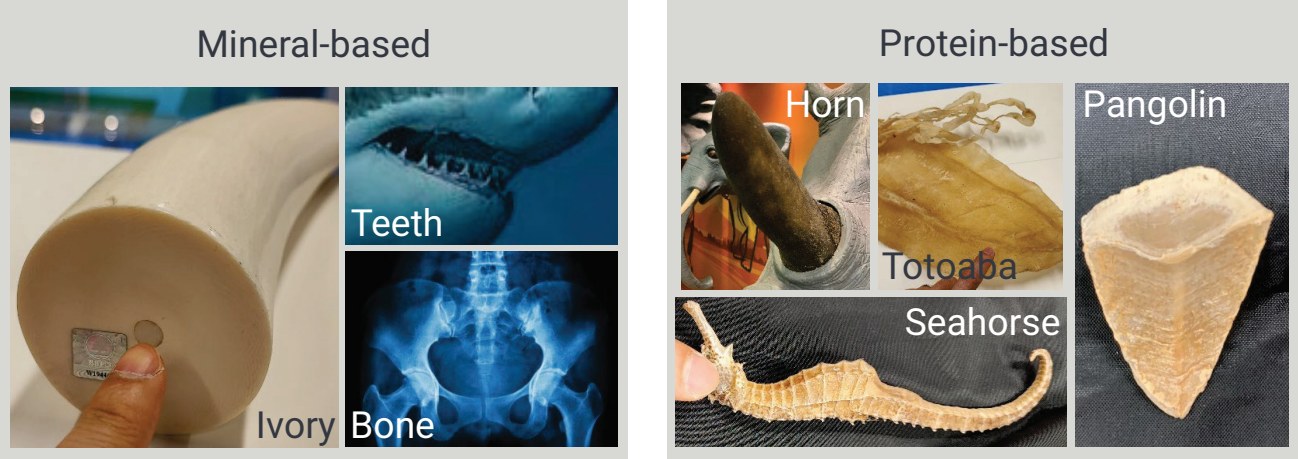

Figure 4. Based on the Raman spectra, the animal products were divided into mineral-based (group 1) or protein-based (group 2) categories.

Samples in group 2 consisted primarily of a layer of keratin, the protein found in hair, nails, and horns. The number of amino acids in different proteins differ and the chemical properties of the 20 possible amino acids vary. However, all amino acids form the same chemical bond, known as an amide bond, when linked together in a protein chain. There are several shared features in the Raman spectra between the protein-based products, arising from this common amide linkage. The intensity of any variation in the spectra depends on the amino acid constituents. If there is sufficient variation in amino acid content, the protein-based products can further be differentiated using Raman spectroscopy.[4] For example, the spectrum for pangolin is sufficiently different from the seahorse spectrum to avoid cross-identification (Figure 5B). This differentiation can be visualized using principal component analysis (PCA) (Figure 6), an analytical tool that helps analysts to see similarities in complex data sets, facilitating interpretation of the results.

In PCA, each measurement is represented by a single point. Points that represent similar measurement values appear closer together, while dissimilar spectral points are positioned further apart. In Figure 6, there are no overlapping points between the seahorse and pangolin data sets, while there are a few points in the totoaba data set that overlap with both the seahorse and the horn sample. However, most of the totoaba measurement points are grouped in a distinct cluster. Overall, the analytical tool shows good differentiation between the four sample types.

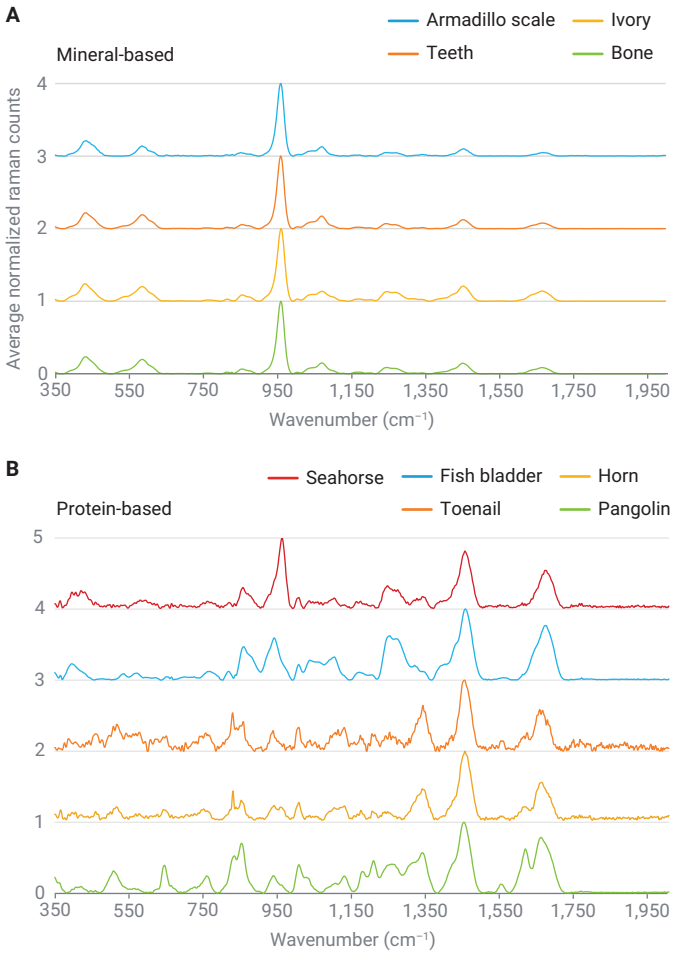

Figure 5. Raman spectra collected using the Agilent Resolve handheld Raman analyzer. (A) Mineral-based samples showing little spectral variation. (B) Spectral variation of the protein-based products.

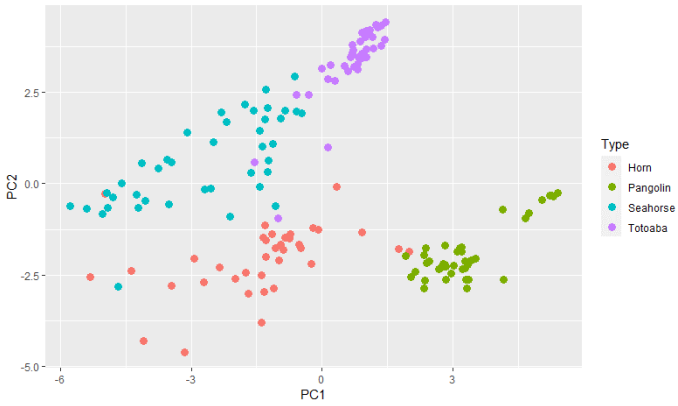

Figure 6. Further separation of protein-based samples using principal component analysis (PCA).

The benefits of Resolve for the identification of other protected endangered species include:

- Fast analysis times with results generated within two minutes enabled the samples to be divided based on their mineral and protein content.
- The high-quality data acquired for the protein-based samples enabled further differentiation and visualization using PCA.
- Operators of the analyzer have the flexibility to create custom libraries that relate to specific materials that are not currently included in the existing on-board spectral libraries.
- No sample preparation or consumables were required for the analysis. Data were acquired by simply pointing and shooting the handheld analyzer at the sample.
- The analyzer can easily be deployed at the location where materials are discovered or stored.

Conclusion

The Agilent Resolve handheld Raman analyzer includes various spectral libraries that enable the identification of a broad range of chemicals and materials. This study has shown the application of the instrument and the SORS technique for the detection of endangered animal species. Using a combination of conventional surface and through-barrier modes of analysis, Raman spectroscopy and SORS technology can be used to:

- Identify ivory through layers of paint and varnish.
- Differentiate plastic substitute materials from authentic ivory and bone.
- Distinguish between mineral-based animal products, such as ivory and armadillo scale, from protein-based animal products, such as rhino horn and pangolin scales.

The simple-to-use Resolve handheld Raman analyzer with SORS capability can provide complimentary data to help detect and identify endangered animal-derived samples.

References

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Further information

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

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