Application Note: 51737

Rapid Screening of Semiprecious Gemstones by Raman Spectroscopy

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Key Words

- DXR SmartRaman Spectrometer
- Array Automation
- Dispersive Raman Spectroscopy
- Gemstone Analysis
- Rapid Screening
- Universal Platform Sampling Accessory (UPS)
- Well Plate Autosampler Toolhead

Introduction

Raman spectroscopy is non-destructive, requires almost no sample preparation and is exquisitely sensitive to crystalline structure and the presence of minor components. For these reasons, Raman is becoming widely recognized as a valuable tool for the analysis of gems and minerals. For high value gemstones, Raman spectroscopy is able to distinguish between genuine and fake specimens and determine whether stones such as diamonds have been artificially treated with high temperature or pressure or with fillers and waxes to enhance their color and raise their value.

Raman is also useful for classifying minerals and semi-precious stones of lesser value. In most cases all that is required is to collect a spectrum and then automatically search a library of mineral spectra to identify the sample. An excellent database well suited to this purpose and consisting of high quality spectral data from well characterized minerals has been developed at the University of Arizona.[1]

This application note demonstrates it is also possible to automate screening and classification of larger numbers of samples by using the Thermo Scientific DXR SmartRaman spectrometer equipped with a Universal Platform Sampling (UPS) accessory and a Well Plate Autosampler toolhead, shown in Figure 1. The DXR SmartRaman spectrometer has been designed specifically for use in routine screening and analysis. The UPS accessory focuses the excitation laser up through a window onto a plane surface. The sample is placed on the sampling window, data collection parameters are automatically optimized by the Thermo Scientific OMNIC software suite, and the spectrum is acquired. The data acquisition can be linked automatically by a macro to search a Raman spectral library for a match. For many samples, the complete analysis can be completed in less than a minute.

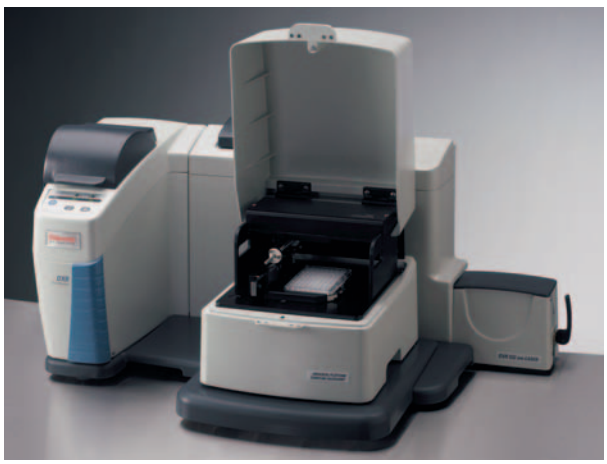

Figure 1: The DXR SmartRaman instrument with the Universal Platform Sampling Accessory (UPS) with the Well Plate Autosampler toolhead installed

Experimental

In this example, we are using the DXR SmartRaman spectrometer configured with the UPS accessory with a Well Plate Autosampler toolhead normally used for analyzing pharmaceutical samples in 96 well plates or custom tablet holders. For this work, we have placed 96 small semiprecious, cut gemstones in the wells of a glass bottom well plate. The wells in the plate have a diameter of approximately 7 mm. Figure 2 shows a picture of the plate containing the gemstones.

The well plate was loaded into the motorized toolhead and a spectrum was acquired from each well. The spectra were acquired using 532 nm laser excitation. Four exposures (5 seconds each) were combined to produce the final spectrum.

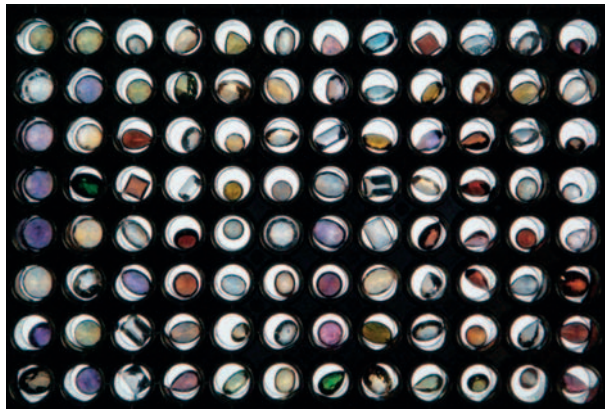

Figure 2: The glass bottomed 96 well plate loaded with semiprecious gemstones

Data Analysis and Results

A large number of analysis techniques can be applied to the 96 spectra in the data set. Below is a list of the techniques available in the Array Automation software, which is part of the OMNIC™ software suite.

Metrics Available for Analysis in Array Automation

- Peak height
- Peak area
- Height above baseline
- Area above baseline
- Quantitative result
- Correlation
- Peak height ratio
- Peak area ratio
- Group analysis
- Cluster analysis
- Principal components
- Multivariate curve resolution

Figure 3 shows a screen capture of the results shown by the software. The results are displayed using a diagram of the well plate. In this example, the wells are color-coded according to the magnitude of peak area above baseline, with red representing the largest area.

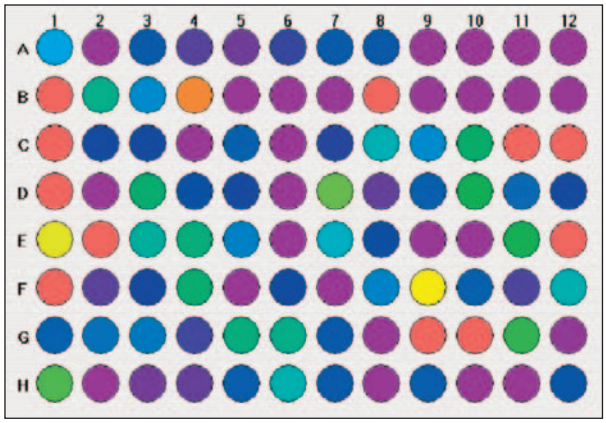

Figure 3: Analysis results of the gemstones, using area above baseline. Red indicates largest area.

Another analysis metric which is simple and very effective is to calculate the correlation between the spectrum of each sample and a reference spectrum from a material of interest, such as a particular type of gemstone. Figure 4 shows the result of performing a correlation between a reference spectrum from topaz and the spectra from each of the samples. Those wells colored red in Figure 4 correspond to samples of topaz. Correlation works well as a means of confirming the identity of a gemstone or set of gemstones.

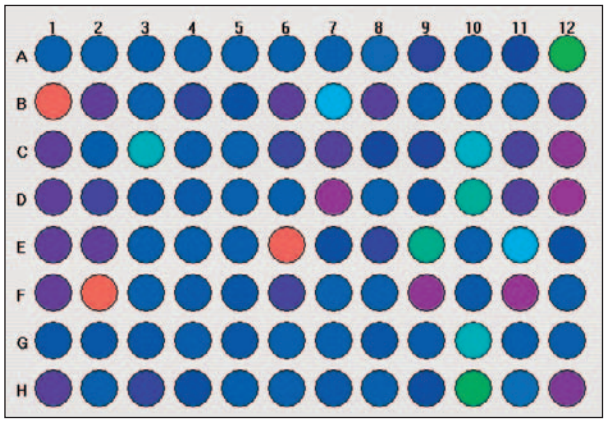

Figure 4: Analysis results of the correlation of the spectra versus a reference spectrum of topaz. High correlation matches are shown in red.

When dealing with unknown samples, spectral searching can be a valuable tool. Figure 5 shows the results of performing a spectral search of the spectrum from well G2 against the reference spectra in the RRUFF spectral library. In this case, we get an excellent match between the spectrum of the unknown sample in well G2 and one of the forsterite spectra in the RRUFF data base. One issue to be aware of in this application is the difference in names commonly used in mineralogy and gemology. Previously, we had used the OMNIC library manager software to add a reference spectrum from a peridot sample acquired in our laboratory to the spectral library. In this case, the three closest matches were from different samples of forsterite, but the match with our peridot spectrum was also very close. A quick check in the literature reveals that peridot is gem quality forsterite. All four matches are correct and a visual examination reveals the yellow green color expected for the stone. A careful examination of the spectra in Figure 5 shows the small spectral differences that are normal in samples of natural gemstones.

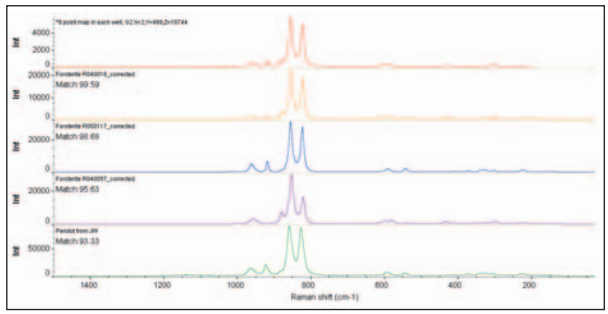

Figure 5: Library results from searching the spectrum of the sample in well G2. High percentage matches to forsterite, including gem quality peridot.

A valuable analysis tool that can be used on a group of spectra is hierarchical cluster analysis. Cluster analysis is a multivariate statistical analysis technique that attempts to assign the spectra to groups based on their spectral similarity. This technique requires no prior knowledge about the samples; it uses a hierarchical approach to assign the spectra to groups starting with the most similar. The results of the hierarchical analysis on the data set are shown in Figure 6. With this technique, there is the ability to adjust the threshold of similarity in order to optimize the cluster results. Once the cluster analysis has been completed and groups determined, the individual wells can be labeled. Figure 7 shows the results after each well has been assigned to a group, noted by the different colors. Placing the cursor over a specific well will result in the well identity being displayed along with the assigned group. The spectra in Figure 8 are examples from the different groups. Spectral searching can then be performed using a representative spectrum from each group. Doing so on the group results in good match values for the following minerals: quartz (citrine, amethyst), beryl (emerald, aquamarine), corundum (ruby, sapphire), pyrope (garnet), zircon, topaz, forsterite (peridot), and labradorite. Thus, a set of samples can be quickly analyzed, grouped and then identified.

The largest group in Figure 7, dark blue, corresponds to wells where the gemstone was not centered over the laser. In those cases, acquiring a single spectrum from the center of the well missed the gemstone. A valuable feature of the Array Automation software is the option to collect spectra from multiple areas in a single well. Figure 9 shows the results that were obtained by collecting a 3 x 3 array of individual spectra in each well by stepping the automated stage in 1 millimeter increments. By acquiring nine spatially separated spectra in each well, a spectrum can be obtained for samples that may be missed by a

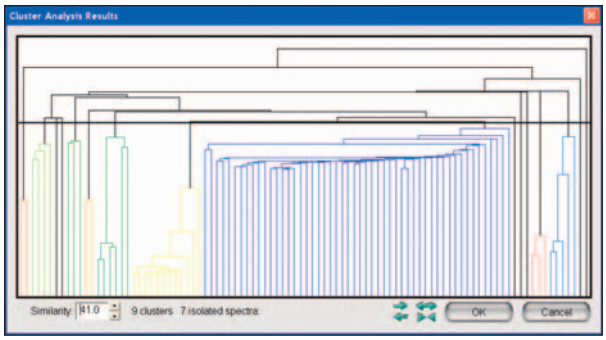

Figure 6: Results of hierarchical cluster analysis on the data set

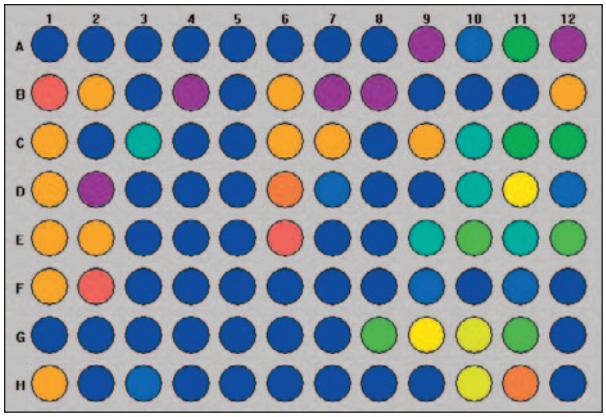

Figure 7: Group assignments based on results of cluster analysis

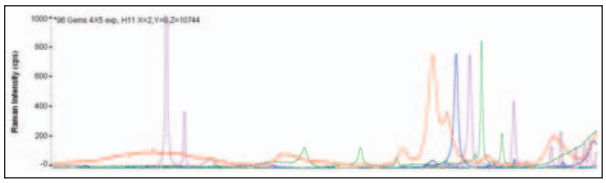

Figure 8: Example spectra from some of different groups

single point collection. Clicking on a well of interest will result in a magnified picture of the well being shown. Figure 9 shows an enlarged image of well C7. By clicking on each of the squares, the individual spectra can be examined.

The resulting spectra from the 3 x 3 array collection can be assigned to groups, as before. Figure 10 shows the new groups determined for the nine-point maps. The same library searching previously described can be performed on the groups. The purple group, well D1 for example, is again identified as quartz. Now, well A1 which was unidentified earlier can be identified correctly as peridot/forsterite, and G3 is now identified as beryl.

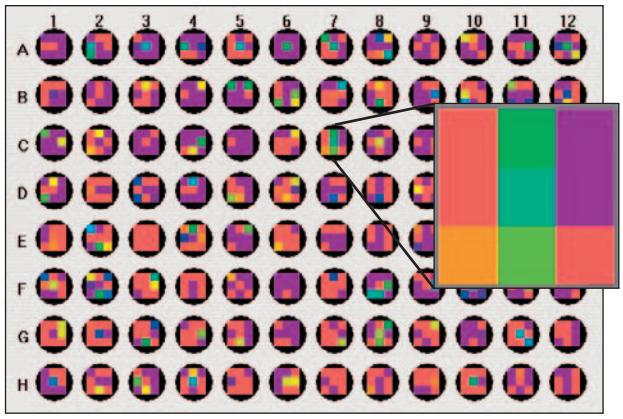

Figure 9: Analysis results of the 3 x 3 array analysis of the 96 wells, using area above baseline with red indicating largest area. Inset shows results for well C7.

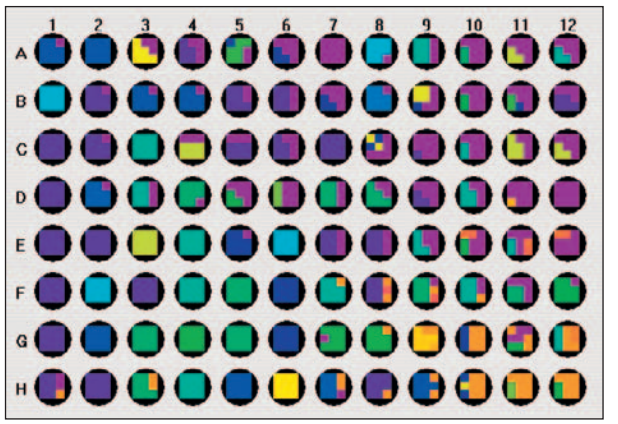

Figure 10: New group assignments using the results from the 3 x 3 array analysis

Conclusions

In this application note, we have described the use of the DXR SmartRaman spectrometer configured with a Smart UPS accessory and the Well Plate Autosampler toolhead for rapid gemstone screening. The DXR SmartRaman instrument, coupled with the sophisticated data collection and analysis capabilities available within OMNIC Array Automation, provides a powerful solution that can be used in many applications where speed and reliability of analysis is required.

References

1. Downs, R. T., (2006) *The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals.* Program and Abstracts of the 19th General Meeting of the International Mineralogical Association, Kobe, Japan.

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