

Raman Microscopy as a Valuable Tool for Failure Analysis

The authors discuss several sample types encountered in their laboratory for which Raman spectroscopy is the only reliable method of analysis. The technique is shown to be a routine and cost-effective tool for the industrial laboratory.

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Raman spectroscopy traditionally has suffered from the misconception that it is a difficult technique to work with, one that is best left to the academics and experimental researchers. Technical advancements in high-performance instrumentation, however, make Raman one of the easiest techniques to run in today's fast paced industrial laboratory. Raman combines ease-of-use features with a non-destructive light scattering technique that eliminates or considerably reduces sample preparation. The result is a new technique for materials analysis that provides definitive answers quickly and easily.

One of the most common questions asked of the failure analyst is, "What is this stuff?" It usually is not a trivial question. In manufacturing environments, unknown materials can stop a production line and cause costly prod-

uct delays. Turnaround time in the lab often is critical, and tools that provide quick answers are invaluable.

In failure analysis laboratories, vibrational spectroscopy techniques for chemical analysis are powerful tools in the identification of unknown materials. They are equally well-suited for verification purposes when the identities of materials in question are known. The vibrational spectroscopy technique Fourier-transform infrared (FT-IR) spectroscopy is well-known even by non-experts in chemical analysis, and typically is one of the workhorses in failure analysis.

Raman spectroscopy is another powerful vibrational technique that can play an important role in the failure analysis lab. Once considered even by experts to be a tedious undertaking, the collection of Raman spectra now is a routine procedure in our laboratories.



Figure 1. Crack section as viewed through the Raman microscope (500x).

Advancements in Raman spectroscopy — such as the implementation of lasers, CCD detectors, notch filters, automatic laser alignment, and unattended calibration routines — make it one of the easiest of techniques to use.

The Failure Analysis Laboratories at Raytheon (McKinney, TX) employ a number of analytical techniques, and recently have begun to take advantage of the unique properties offered by Raman spectroscopy. This article presents a few examples where Raman is shown to be an indispensable analytical tool.

Analysis of Difficult Samples

Raman spectra routinely are collected in our chemical analysis lab using Thermo Electron's Nicolet Almega dispersive Raman spectrometer, which is equipped with dual lasers (a high-brightness 25-mW, 532-nm laser, and a 30-mW, 785-nm laser) and both micro and macro sampling capabilities. To provide spectral integrity, a calibration routine is run automatically once a week during off-hours and is verified periodically throughout the week using the integrated reference polystyrene standard.

Raytheon added Raman spectroscopy to its arsenal of analytical techniques because it addresses limitations found in other techniques. These limitations result from both sample and method limitations, as illustrated below. An important advantage to Raman spectroscopy is what is commonly referred to as spot size. Electronic components are becoming smaller, and the materials under investigation also are becoming smaller and much more difficult to analyze. Using a lower limit spot size of about 1 μm , Raytheon analysts have been able to

identify materials previously inaccessible by other methods.

Most chemical analyses require some manipulation of the sample, such as isolation (removal) from its surrounding background, and in the case of some techniques, even complete sample destruction. Raman's advantage is its ability to analyze samples "as is," that is, without modification. Frequently the lab is asked to perform analyses of small particles without manipulating the parent component in any way — an extreme example of the requirement for non-destructive analysis. Even in cases where spectra possibly could be collected with infrared microscopy without manipulating the material, the analysis often is hindered by the substrate on which it resides, the so-called "background." With Raman microscopy, background considerations, such as the presence of reflective surfaces, are nonexistent. In addition, Raman often can be performed directly through glass or plastic packaging for truly noninvasive sample handling.

Examination of a Cross-Sectioned Sample

Cross sectioning of electrical components, circuit boards, and many other types of parts is perhaps one of the most common practices of failure analysis. Often, the analyst is asked to characterize the materials revealed by the sectioning process. With FT-IR methods, sample preparation usually requires removing the materials from the section for analysis. In the case of electronic components, the areas in question often are too small to allow for adequate removal, and the analysis cannot be performed.

The following case illustrates an example in which Raman microscopy proved

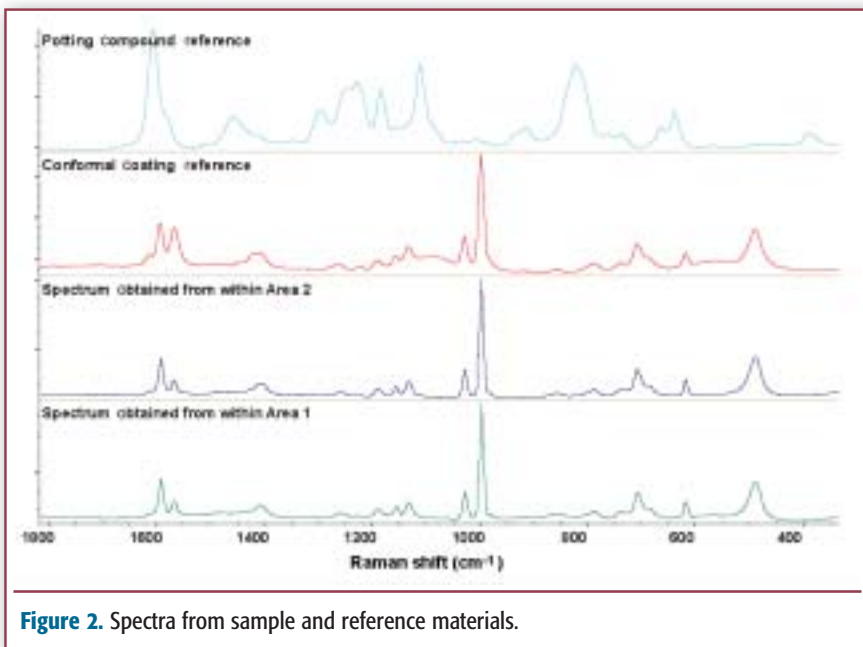


Figure 2. Spectra from sample and reference materials.

invaluable. A braze joint crack was sectioned to determine the depth of penetration. Also, the lab was asked to determine whether a silicone conformal coating had seeped into the crack and, if so, how deep. The reasoning for this request is that if silicone was present in the crack, it was formed before the component was covered with uncured liquid conformal coat. On the other hand, if the crack simply contained free space, it formed after the conformal coating cured.

In this analysis, size limitations, as well as background concerns, prevented spectra collection using infrared microscopy. The second spectrum in Figure 2 is a reference spectrum of the conformal coating, the bottom two are spectra from the areas specified in Figure 1, and the top spectrum is of the epoxy potting compound used in the sectioning process.

As indicated by these spectra, the lab was able to show that conformal coat-

ing was in fact present in the crack and by further sampling at different areas of the crack, we were able to determine the depth of penetration. The 532-nm laser was used in this case and provided an excellent response, as this sample exhibited little fluorescence.

Raman as a Confirmatory Technique

The old idea that one data point has value, two is better, three is even better, etc., is well known to analytical scientists. The ability to generate additional sample information — for example, data points — using Raman methods has proven to be of great value to our labs. For example, the lab was presented with a somewhat odd failure: magnetically actuated clutches that passed all testing upon shipment were found to be inoperable after storage for about six months. The clutches were stuck and would not move



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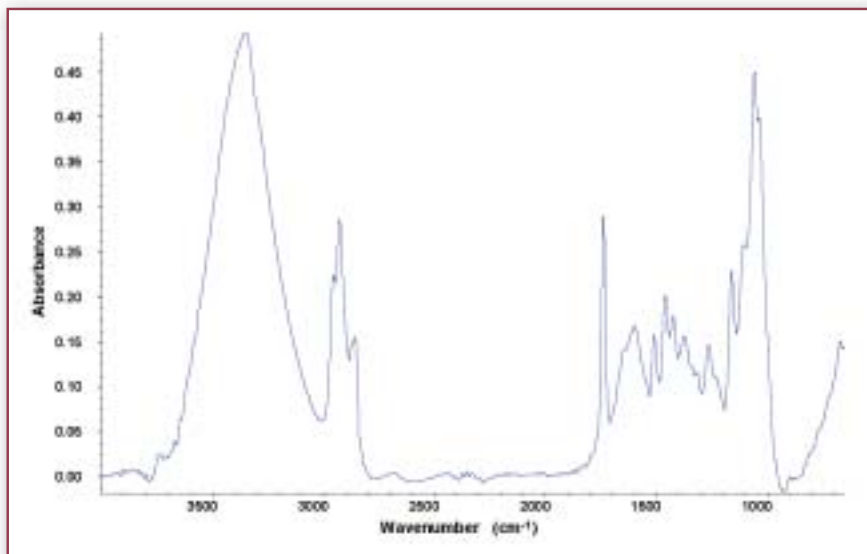


Figure 3. FT-IR spectrum indicating a carbohydrate material in lubricant.

on the shaft. Disassembly revealed that the clutches could be broken free and restored to operating conditions by pulling the clutch loose with a few pounds of pressure. Initial investigations revealed solid clear particles in the grease. Infrared spectroscopy provided the spectrum shown in Figure 3.

The spectrum has strong indications of a carbohydrate material and was dismissed initially as a common contaminant such as cotton fibers. However, upon further investigation, spectra were collected that suggested sucrose (table sugar). As this seemed very unlikely — not to mention a hard sell to the supplier — Raman spectroscopy was chosen for verification purposes. An added advantage of this method was that individual crystals could be analyzed as is on the parts and maintained for the supplier's later inspection. In this case, spectra were collected using both Raman lasers so that three independent data points could be obtained.

As mentioned, finding sugar in a lubricant was unexpected. We initially were very skeptical and tried to confirm these findings. Upon collection of the Raman data, it became obvious that these particles were indeed sugar (Figure 4). In this case it should be pointed out that the richness of the Raman data, as revealed by the multitude of bands, also was an advantage when compared with the infrared data.

After consultation with the supplier, we learned that the assembler was permitted to drink coffee, with sugar dispenser nearby, in the assembly area. Further investigation verified that the mechanism of slow crystallization of sugar crystals between the clutch and shaft led to the observed failures.

Size Limitations and the Value of a Two-Laser System

This example illustrates the value of having two excitation lasers on a mod-

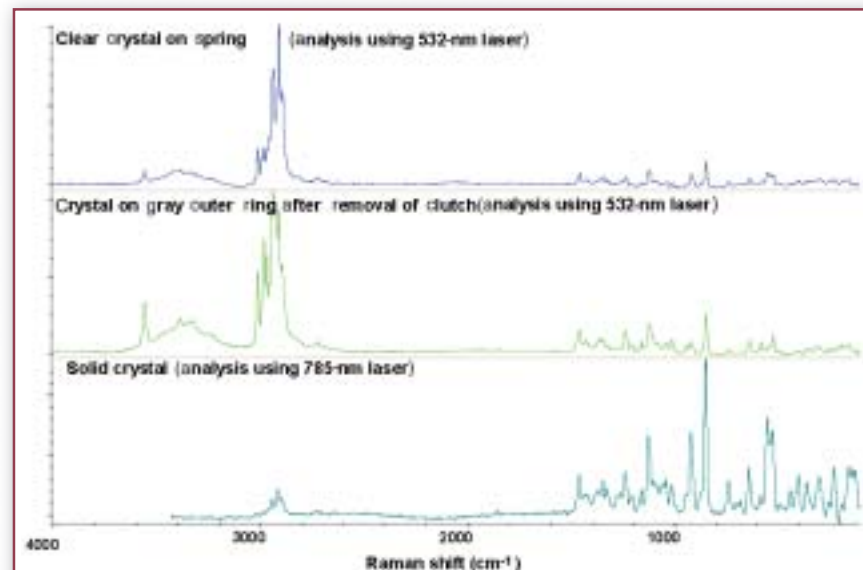


Figure 4. Corresponding Raman spectra of sugar crystal (high matches from both lasers).

ern Raman system, as well as further demonstrating the small spot size capabilities of Raman in general. In this case the lab was presented with a wafer composed of a complicated stacking of materials.

The red arrow in Figure 5 points to the specific area of analysis. The residue is far from obvious in this image and can be observed only under high magnification. We determined the residue to be an irregular shaped material with dimensions of about 1–4 μm , depending upon direction of measurement. It also was found to reside within a cavity formed around the various stack-up layers.

Complicating matters was the request that the sample not be altered in any

way. We attempted infrared microscopy, but were unsuccessful as a result of both spot size limitations and the fact that the

sample presented a poor background for collection. This challenge appeared an ideal candidate for Raman, and is an example of one of our primary reasons for obtaining this capability — small spot size.

Initially attempts were made to collect the spectra using the 532-nm laser. Our experience has been

that the shorter excitation wavelength generates a stronger Raman signal, making it our first choice. However, in this example, as well as others we have encountered, intense fluorescence made analysis with the 532-nm laser impossible. As a result, further examination was made using the longer wavelength and

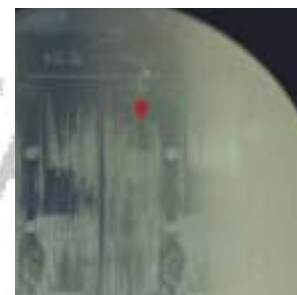


Figure 5. Photograph of 6-in. diameter wafer.

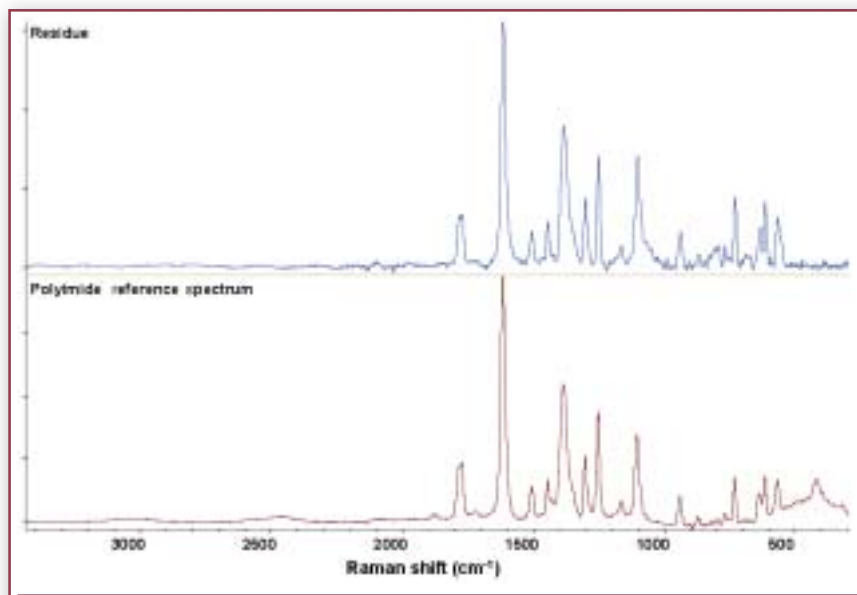


Figure 6. Polyimide spectrum collected from wafer and spectral match to internal database standard.

less Raman-active 785-nm laser. Quickly overcoming the fluorescence problem, we collected a high quality spectrum identifying the residue as a polyimide (Figure 6). While this example is seemingly mundane, it effectively highlights the spot-size advantage offered by Raman spectroscopy. Many times in such cases there are simply no suitable alternative methods.

Summary

The examples presented here illustrate many of the advantages that modern Raman microspectroscopy instruments offer to any laboratory performing materials identifications. Modern Raman instrumentation clearly has matured to the point where it is an applicable and cost-effective method for investigation in the industrial failure analysis laboratory.

One of the successes of Raman spectroscopy is its ability to characterize materials that previously were intractable with our existing instrumentation. Conclusions were drawn from conjecture and supposition, lacking the strong spectral data provided by Raman spectroscopy. We have no doubt that the cost savings provided to us by having more reliable answers in a more timely fashion have paid for the system in very short order.

More surprising, from our point of view, is the expanded role that this instrument now plays. While we anticipated that Raman would enhance our lab's existing analytical capabilities, the rapidity of results and ease of use make the modern Raman microspectrometer a primary analytical tool in our laboratories. ■