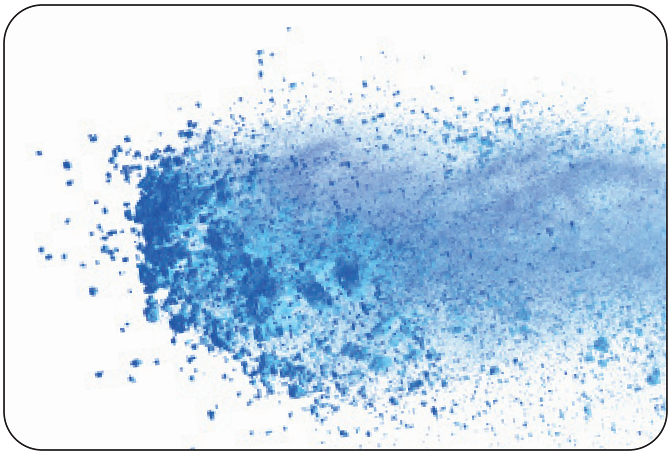

Application Note AN R530

Particle Analysis by Raman Microscopy

There are many occasions where analyzing unknown particles can be important. Examples include illicit drug analysis, particulate adhesions occurring in a recycling process, electronics manufacturing, particles in liquid biomedical products, and many more. Further, the identification of unknown particles can be extremely important in reverse engineering products and identifying the cause of failure in the manufacturing process. One of the challenges to analyzing particles is that the size of the particles can be very small and potentially embedded in a matrix. Particle defects can adversely affect product quality, appearance, and performance.

Keywords	Instrumentation and Software
Particles	SENTERRA II Raman Microscope
Inclusions	OPUS Spectroscopic Software
Failure analysis	OPUS SEARCH Spectral Identification Software
Electronics	Spectral Databases
Forensics	
Pharmaceutical	

When performing particle analysis, Raman microanalysis is of advantage compared to IR spectroscopic analysis for a couple of reasons. First, Raman microscopy is contactless and non-destructive allowing the sample in question to be analyzed without concern for carry-over, alteration or damage. This is particularly important in forensic and pharmaceutical investigations. Infrared analysis utilizing direct reflectance yields a weak signal and ATR analysis requires direct contact with the sample. Because the excitation illumination for Raman spectroscopy is typically in the visible, the achievable lateral resolution of better than 1 µm is clearly smaller than can be achieved by infrared microscopy.

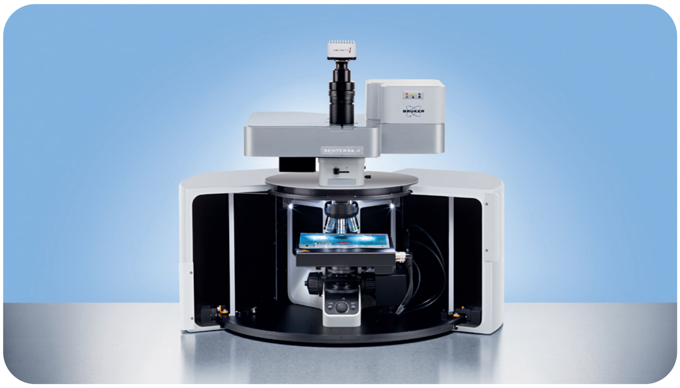

Figure 1: SENTERRA II Raman Microscope.

Furthermore, confocal Raman microscopy can be utilized to collect the spectrum of the particle of interest while rejecting the surrounding matrix. This allows the analysis of particles to be readily conducted though polymer bags, vials, or cover slips on glass slides.

The new SENTERRA II (figure 1) is the ideal tool for the non-destruc-tive analysis of particles. The novel Wizard software inter-face in the OPUS software provides a user friendly platform that guides the user through the entire sample analysis process. This process begins with the visualization of the sample utilizing state-of-the-art optical microscopy techni-ques such as polarized light, Koehler illumination, darkfield illumination, and more. The optical microscopy capabilities are important in characterizing the physical properties of the sample (color, shape, morphology, etc.). After capturing visible images, the Wizard takes the user to the spectrosco-pic part of the software for quick and easy optimization of the collection parameters, as shown in Figure 2. Clicking on the next button in the Wizard takes the user to the data acquisition interface where the data acquisi-tion points, lines, or areas are defined. Depth profiling is also readily configured in the dialog. The SENTERRA II includes the ability to conduct fast imaging, where thousands of spectra are collected in seconds.

Screen shot from OPUS software

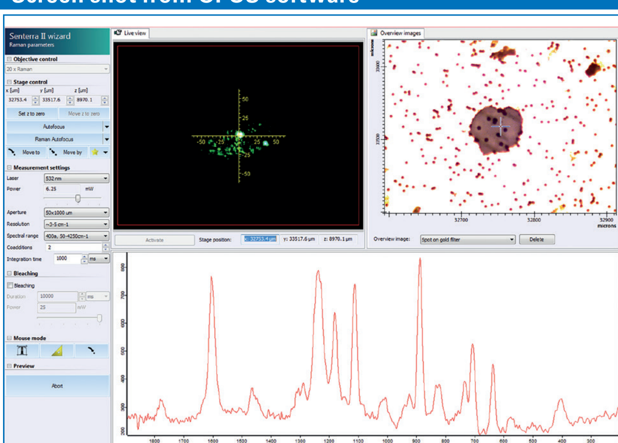

Figure 2: Screen shot of the Bruker's OPUS software Raman micro-scopy Wizard interface. In this dialog, data collection parameters are easily selected.

Upon completion of the data collection, the analysis is rea-dily accomplished in OPUS. An array of data analysis tools is available for quickly identifying unknowns and rendering their respective distributions. These analysis tools encom-pass basic functions such as integration and library sear-ching to more advanced evaluation methods, such as factor analysis, cluster analysis, functional group profiling, mixture analysis, and many more.

Example 1 - Raman analysis of particle contaminants found on an electronics circuit board

Particle contaminants have been a long standing problem n the manufacture of semiconductor wafers and circuit boards. These contaminants can adversely affect product performance and reduce product lifetime. Such particles can be very small (on the order of a few microns) and chal-lenging to analyze. Figure 3 (top) shows the Raman spectra collected from two particles found on circuit boards in a manufacturing plant. The data was collected with 785 nm laser excitation at 4 cm^{-1} spectral resolution for one minute utilizing the confocal mode of the SENTERRA II Raman microscope with a 50x 0.75 NA objective. This high quality Raman data was collected non-invasively without needing to touch the particles. Non-invasive infrared microanalysis would not be possible, as ATR (which works by having direct sample contact) must be used on particles that are this small. Figure 3 (bottom) shows the visible images of the particles and the corresponding Raman spectra after fluo-rescence removal using Bruker's patented concave baseline correction function.

RAMAN spectra

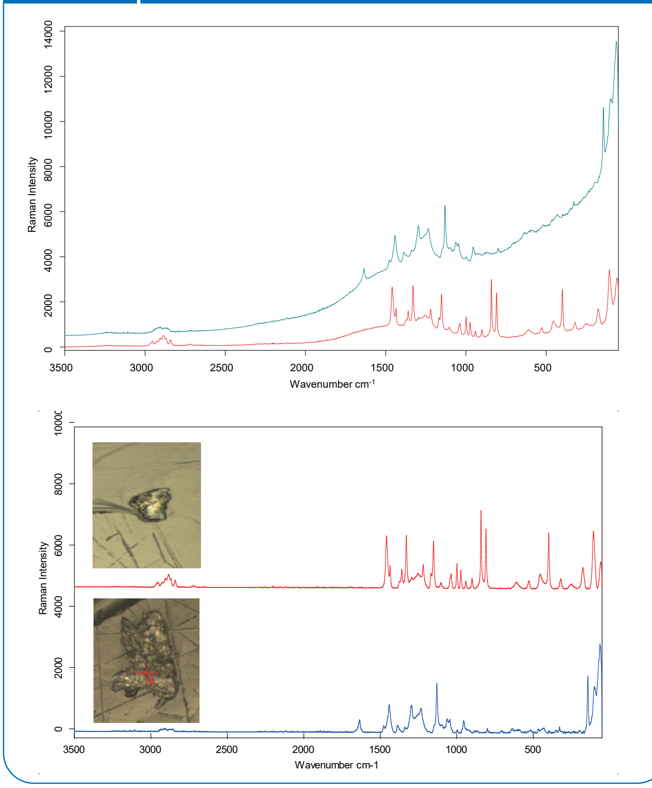

Figure 3: top: Raw Raman spectra collected from two real world contaminants found on a semiconductor product.

Bottom: Spectra after fluorescence removal. Visual images of the respective particles are also shown.

Example 2 - Analysis of illicit drug particles without breaking the chain-of-custody

During a crime scene investigation, investigators place evidence found at the crime scene in polymer bags and seal the bags. Optimally the bag stays sealed throughout the investigation, so no question can be raised later about evidence integrity. To subsequently analyze such evidence using commonly employed analytical tools under this constraint can be very challenging. Confocal Raman microscopy is the analytical tool most suited for this type of analysis. Confocal Raman microscopy allows the impinging excitation laser light to be focused on the areas of interest, as determined by the utilization of polarized light and/or fluorescence illumination. The signal from the bag is essentially completely rejected in this mode and only the spectrum of the compound in question is collected. The Raman spectrum of methamphetamine, as shown in Figure 4, was collected from trace evidence found in a suspect's toilet. In this case, the Raman spectrum was collected through two bags, the bag containing the powder particles and the chain-of-custody bag. The experimental parameters were the same as in Example 1 excepting the use of a 0.4 NA 20x objective.

Raman spectrum

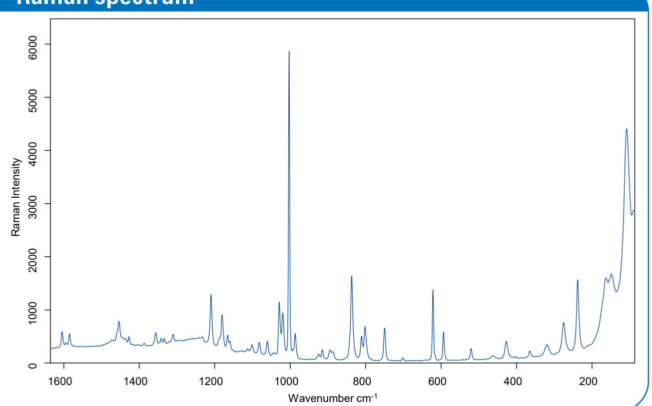

Figure 4: Raman spectrum of methamphetamine collected through a chain-of-custody bag used by crime scene investigators.

Example 3 – Identification of particulate adhesions of recycled carbon fiber material

Carbon fiber reinforced polymers (CFRP) are high-tech composite materials consisting of a polymer matrix and carbon fibers as reinforcement. Due to their light weight and extraordinary stiffness, CFRP's are increasingly being used in many high end products such as care sporting goods and aerospace industry, just to name a few.

For this reason the recycling of composite materials is becoming more and more important. A promising innovative method is electrodynamic fragmentation. Electrodynamic fragmentation allows the separation of composite materials into their component parts. This process is based on the selective break up of solid materials with ultra-short underwater pulses with high energy spark discharge. One of the advantages of this technique is the recovery of carbon fibers for genuine use [1].

Raman microscopy is a non-contact analytical method, which can be important for process optimization. Here, the microscopic inspection of the recycled carbon fiber material reveals various unknown particulate adhesions. Obviously, these contaminations (Figures 5a and 5b) were generated during the recycling process. The Raman spectra of the contaminations were collected with a 532 nm laser and the use a 100x0.9 NA microscope objective.

By applying an automated search of the Raman spectra in a digital library, small particles in the range of less than 1 µm could be identified as calcium carbonate (Figure 6a). The process water was suspected as a potential source of the inorganic contaminant.

A larger contamination with a diameter around 5 µm was identified as polyvinyl pyrrolidone (Figure 6b). The origin of this polymer was sourced to abrasive material from the transportation system. For comparison a typical Raman spectrum of carbon fiber is displayed in Figure 6c.

Raman spectra of particulate adhesions on carbon fibers

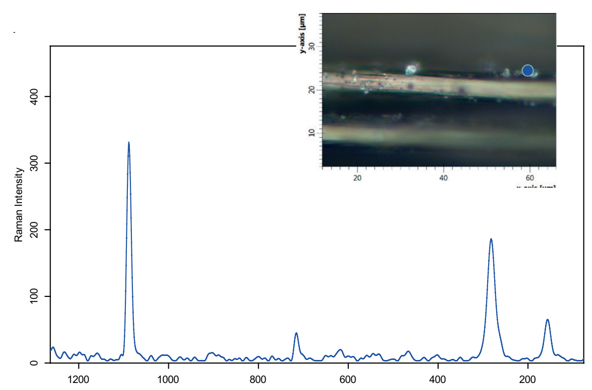

Figure 5a: Image and Raman spectrum of a particle with diameter of less than 1 µm.

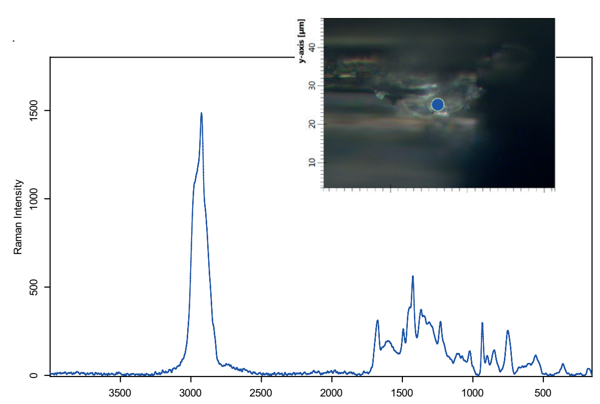

Figure. 5b: Visible image and Raman spectrum of a particulate contaminant with a diameter of less than 1 µm.

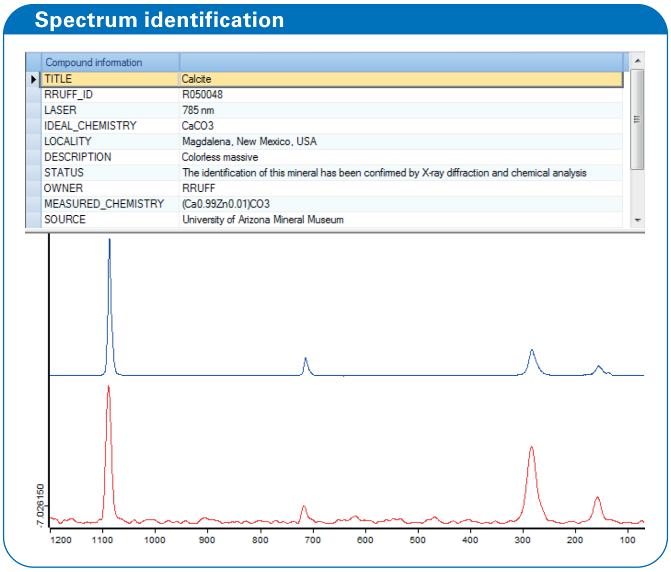

Figure 6a: Identification of inorganic particles as calcium carbonate by library search.

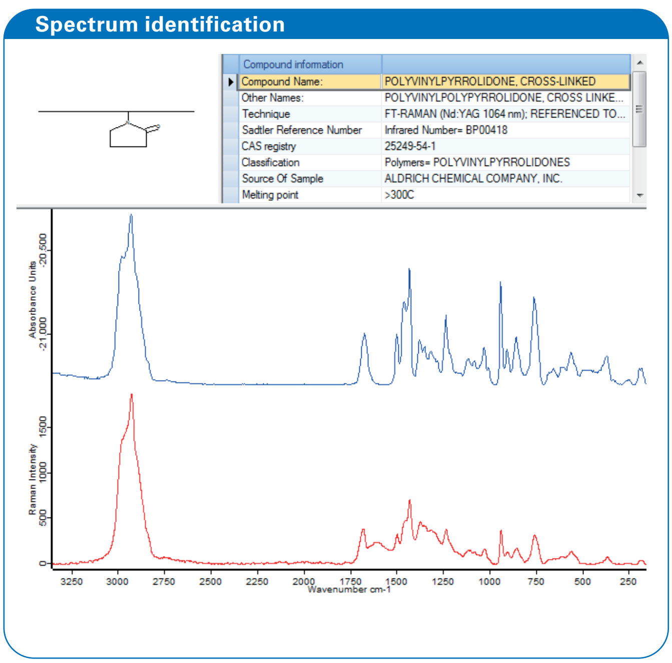

Figure 6b: Library search of polymeric particle revealing polyvinyl pyrrolidone

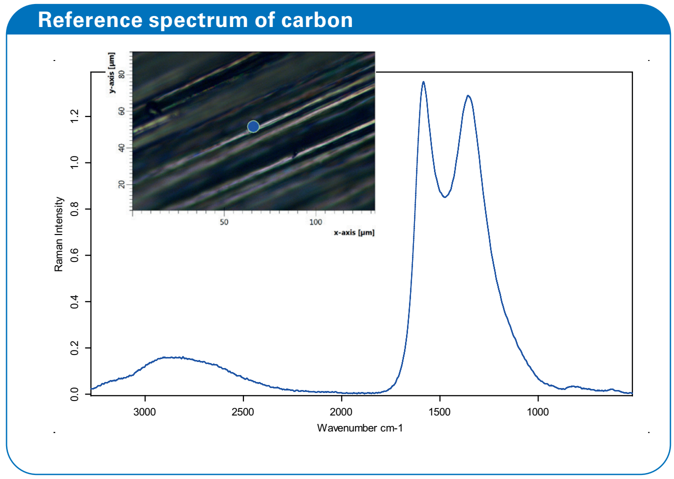

Figure 6c: Visible image and a typical Raman spectrum of carbon fiber.

Conclusions

The SENTERRA II is a powerful tool for the analysis of particles without sample preparation even within sample containers or as microscopic adhesions attached to an optically opaque fiber material. Due to its confocal design and high lateral resolution, the analysis of submicron particles is readily accomplished. Extensive Raman spectral data bases with more than 28,000 Raman spectra are available for unambiguous identification of unknown materials.

References

[1] C. Karlstetter, Fraunhofer Institute for Building Physics, Valley, Germany, http://www.ibp.fraunhofer.de/content/dam/ibp/en/documents/Information-material/Departments/BBH/Produktblaetter/IBP_087_PB_Bauchemie_Fragmentierung_03_web_en.pdf

Figures and images 5 and 6 are courtesy of Mrs. Anna-Lena Hoehn, Fraunhofer Institute for Building Physics,Valley, Germany

Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 439-9899
info.bopt.us@bruker.com

Bruker Optics GmbH & Co. KG

Ettlingen · Germany
Phone +49 (7243) 504-2000
info.bopt.de@bruker.com

Bruker Shanghai Ltd.

Shanghai · China
Tel.: +86 21 51720-890
info.bopt.cn@bruker.com

www.bruker.com/optics