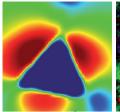
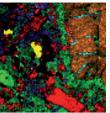




Raman Spectroscopy

## **Introduction to Raman Imaging**





Technical Note
TN RA-05

Raman imaging is a powerful technique for generating detailed chemical images based on a sample's Raman spectrum. A complete spectrum is acquired at each and every pixel of the image, and then interrogated to generate false colour images based on the material's composition and structure.

Raman imaging is widely used to characterize the distribution of components within a sample, but additionally it is sensitive to material concentration, phase, stress/strain, and crystallinity. With a single data set a wide variety of Raman images can be created which take the researcher well beyond what the eye can see.

Raman imaging can be carried out in all three dimensions (X, Y and Z) in any desired combination. Perhaps the most common Raman imaging is 2D surface imaging (XY plane), but other configurations are available, including 1D depth profiling (Z axis), 2D optical cross-sectioning (XZ and YZ) and full 3D volume imaging (XYZ). In addition, Raman imaging can be combined with other measurement protocols, such as kinetic studies, or temperature ramping.

High quality, high precision Raman images require high spatial resolution (referring to the optical resolution, the power to distinguish closely placed objects). HORIBA Scientific's confocal Raman microscopes offer true diffraction limited spatial resolution down to sub-micron regimes, depending on the system configuration (e.g. laser wavelength, and the numerical aperture of the objective lens). The confocal design affords the necessary axial (depth) resolution for depth profiling, optical cross-sectioning, and 3D volumetric imaging.

20 µm

3D volumetric image of an expanded polymer bead within a polymer matrix.

The immersion objective oil is also shown.

[Data courtesy of Dr Neil Everall, Intertek Wilton, UK]

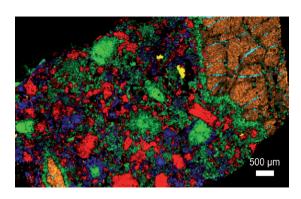
In combination with atomic force microscopes (AFM), *tip enhanced Raman spectroscopy* (TERS) routinely offers spatial resolution down to 15 nm and below, well beyond the optical diffraction limit.

It is important to employ a high precision stage to accurately and automatically move the sample for the measurement. A mechanical motorized stage travels long distances, typically in the order of tens or hundreds of millimeters with step sizes below 50 nm (often referred to as 'resolution' in specification sheets), suitable to image large objects such as tablets, meteorites and minerals, tissue sections and filters. Alternatively, a piezoelectric stage covers short distances, typically a few hundreds of micrometers, with nanometer step resolution, ideal for imaging nanomaterials such as carbon nanotubes and quantum dots. A piezo stage can be used with any Raman microscope, and is necessary for an AFM coupled Raman microscope.

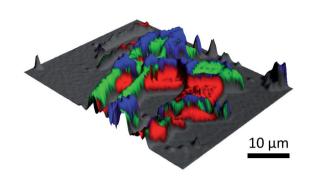
Additional imaging options include SWIFT<sup>TM</sup> for ultra-fast Raman imaging, and DuoScan<sup>TM</sup> for adaptive measurement size. SWIFT<sup>TM</sup> reduces the total measurement time drastically, allowing the acquisition of a large number of spectra in a very short time. DuoScan<sup>TM</sup> enlarges the measurement area per spectrum without compromising the confocality, ideally suited to macro imaging of large samples.

Translating the raw data (a collection of spatially resolved Raman spectra) into images, as displayed in this technical note, requires a software for processing, analysis and visualization.





Large area map covering a 7mm x 5mm of a meteorite thick section, highlighting distribution of enstatite, forsterite, anorthite, whitlockite, rhodonite and carbide species.



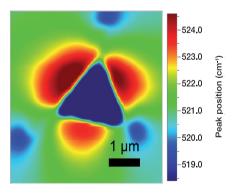
Layered graphene structures showing total graphene G-band intensity (surface), with distribution of silicon substrate and mono-layer, bi-layer and tri-layer graphene.

A Raman spectrum contains the information on material identity (e.g. characteristic Raman bands), material composition (e.g. peak intensity or multivariate analysis scores), molecular structure or strain (e.g. peak position), crystallinity or phase (e.g. peak width), and more. HORIBA Scientific's LabSpec 6 spectroscopy suite offers comprehensive functionality including multivariate analysis (MVA) to distill this information from the spectral data into scientifically meaningful images.

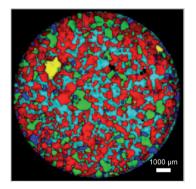
A 2D image such as a surface image or an optical cross section uses image color or brightness to express the chemical or structural variation in the sample. A set of colors or range of brightness are assigned to represent a range of intensity or peak position/width via a look-up-table (LUT). Sometimes a 2D image is rendered in 3D, plotting the intensity, peak position/width, bandwidth, or height (e.g. AFM topograph) along the

third axis, for the best visualization. A true 3D image dataset such as a volume image uses three display axes and a LUT to convey the chemical or structural information; software display with rotation and transparency control allows the image to be fully visualized, to understand both internal and external structure.

Raman imaging is a powerful tool for analytical scientists in many varied fields. It is widely used for micro- and nanoscopic detailed visualization of chemical structure, including characterizing pharmaceutical API distribution and uniformity, mineral structure, graphene layer structures, cabon nanotube size and conducting properties, strain in semiconductor devices, polymer coatings, and biological tissue sections and cells. As new materials and new research fields develop, confocal Raman imaging has the ability to offer new insights to material structure and properties.



Map of Berkovich nano-indented Silicon, illustrating peak shift caused by local strain around the indent region.



Sectioned pharmaceutical tablet analyzed with DuoScan™ macrospot for 100% coverage of sample surface, showing distribution of main active and excipient ingredients.





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**USA:** +1 732 494 8660 **UK:** +44 (0)20 8204 8142 **China:**+86 (0)21 6289 6060 France: +33 (0)1 69 74 72 00 Italy: +39 2 5760 3050 Brazil: +55 (0)11 2923 5400

**Germany:** +49 (0)89 4623 17-0 **Japan:** +81 (0)3 6206 4721 **Other:** +33 (0)1 69 74 72 00

