Molecular and Microanalysis

Spring 2007

This newsletter is produced by HORIBA Jobin Yvon's Molecular & Microanalysis Team, to provide our customers, colleagues & friends with up-to-date information in the fields of Raman, Fluorescence and XRF Instrumentation and Applications.

See us next at:

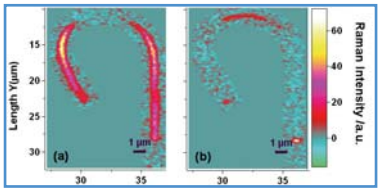
PITTCON 2007

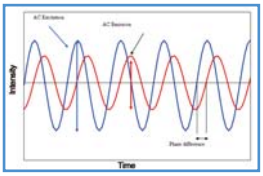
The Molecular and Microanalysis Update will continue to include applications articles by our customers, technical advice, news and information on seminars and conferences. We hope that you find the new update as informative and useful as its predecessor.

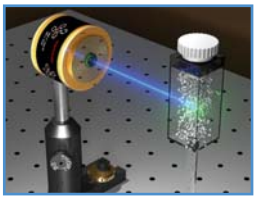
Welcome to the first edition of the "Molecular and Microanalysis Update"

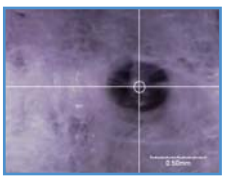
This publication is an extension of the Raman Update which we have been publishing for a few years now. With the formation of the Molecular and Microanalysis Division at HORIBA we have taken the obvious step to expand our Update newsletter to include application and product information from all instruments manufactured under the new division. The Molecular and Microanalysis Division incorporates our Raman, fluorescence, photoluminescence, cathodoluminescence, FT-IR and EDXRF instruments. We are excited by the formation of the Molecular and Microanalysis Division as it focuses our efforts at HORIBA in the areas of molecular spectroscopy, microanalysis and imaging. As a division we will continue to provide the high performance instrumentation expected from HORIBA as well as developing exciting new products that will enhance analytical science.

The Spring edition :









Raman Imaging of a Single GaN Nanowire:

Pushing the limits of Confocal Microscopy

François Lagugné-Labarthet and David Talaga
Institut des Sciences Moléculaires, CNRS-Université Bordeaux 1, France

One-dimensional semiconductor-nanowires of the wide-bandgap gallium nitride (GaN) are prime candidates for nanoscale devices such as short wavelength emitter optoelectronic devices and high-power/high-temperature electronics. Subsequently, it is of importance to measure the homogeneity and the composition of such nanowires at the individual scale and to correlate them with the dimensions and optical properties of these strongly anisotropic materials. In the present work, we have conducted high resolution Raman measurements on a single GaN nanowire using a confocal microscope in conjunction with a high resolution piezoelectric stage for an accurate and reproducible positioning.

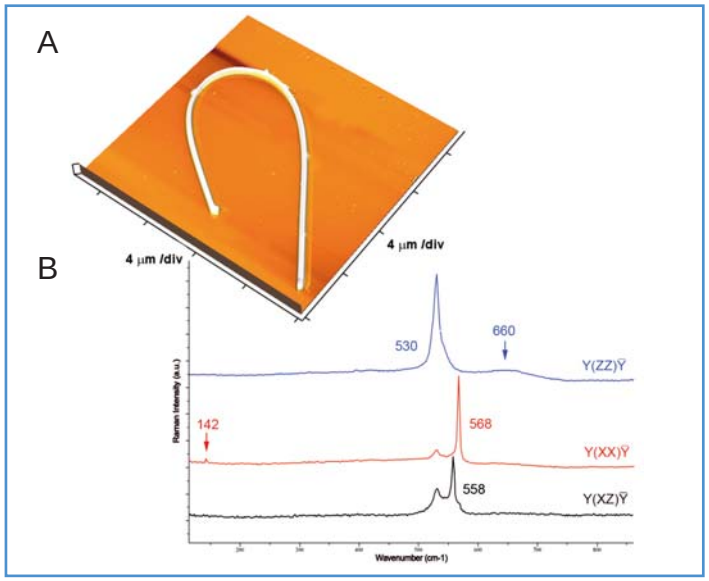


Figure 1: Cross section (a), atomic force microscopy topographical image (b) and polarised Raman spectra of the [001] GaN nanowire deposited on a glass substrate

A single [001] nanowire with a Wurtzite-like hexagonal cross section was first cut and positioned on a microscope glass slide. Atomic force microscopy (AFM) reveals a diameter of about 170 nm and a length of 41µm (Fig.1). Our Raman instrument is based on an inverted microscope (Olympus IX 71) combined with a LabRAM (HORIBA Jobin Yvon) spectrometer (grating 600 grooves/mm, resolution 4 cm^{-1}). The sample was scanned with a piezoelectric stage with an intrinsic accuracy of about 1 nm in the lateral directions. The light beam input excitation wavelength was fixed at λ=514.5 nm from an Ar^+ ion laser and the input polarization was selected with a half-waveplate. Focussing on the sample was done with a 100X objective (Olympus MPL 100X-NA=0.90) and an analyzer just in front of the entrance slit of the spectrometer to measure the Y(ZZ)$\bar{Y}$, Y(XX)$\bar{Y}$ and Y(XZ)$\bar{Y}$, and polarized spectra. For GaN single nanowire, four main signals are observed at 142, 530, 557 and 568 cm^{-1} and they can be assigned to E_2(low), A_1(TO), E_1(TO) and E_2(high) symmetry type modes, respectively (Fig.1).

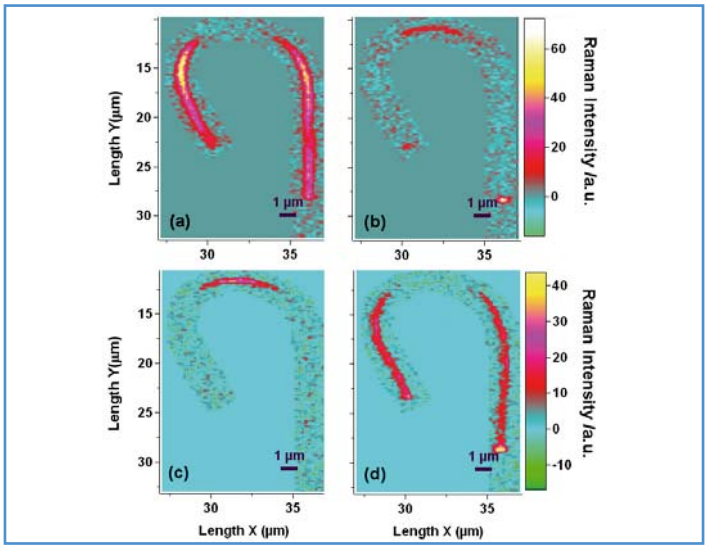
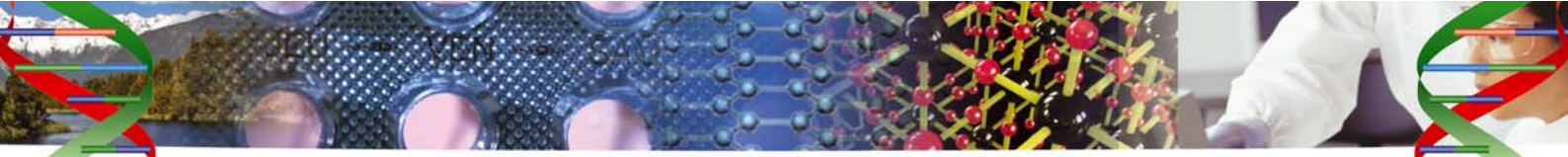


Figure 2: Polarised Raman images generated by integration of specific polarised modes for Y(ZZ)$\bar{Y}$ and Y(XX)$\bar{Y}$ configurations.

Mapping of the nanowire was performed by recording step-spectra at every 200 nm with an integration time of 1s. By intensity integration of the [509-552 cm^{-1}] spectral domain around the A_1(TO) mode (530 cm^{-1}), the variations of the Raman signal over the full nanowire are investigated (Fig.2). The images show a lateral resolution better than 200 nm. For the polarization configuration, fig. 2 shows that the signal is maximum on the straight portions of the nanowire, while it almost disappears on the bent portion of the nanowire. In Y(XX)$\bar{Y}$ polarization configuration, the opposite spectroscopic contrast is observed with a maximum signal of the 568 cm^{-1} mode in the straight portions of the wire as observed in figure 2 and a maximum signal for the A_1 mode in the horizontal part of the nanowire.

Reference: "Polarized Raman Confocal Microscopy of Single Gallium Nitride Nanowires", P.J. Pauzauskie, D.Talaga, K. Seo, P.Yang, F.Lagugné-Labarthet, J. Am. Chem. Soc., 2005, 127(49), 17146.



The MF² : A Revolution in Fluorescence Dynamics

Dr Jim Mattheis, Fluorescence Applications Manager,
HORIBA Jobin Yvon Inc, Edison, NJ, USA

The HORIBA Jobin Yvon molecular and microanalysis team introduces a new and novel instrument: the MF². Fluorescence scientists now have an important set of tools to help understand natural processes. The MF² is based on unique technologies, which increase data collection rates by 10,000 times and dynamic range by 1000 times over conventional approaches!

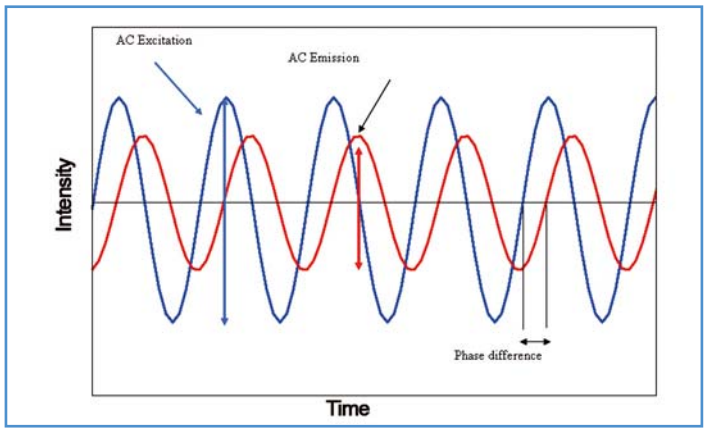


Figure 1a: Relationship between modulated excitation beam (blue) and the resulting modulated fluorescence emission (red).

Fluorescence methods offer sensitivity, selectivity and wide time resolution. With HJY instruments we can measure the duration of molecular events from picoseconds to nanoseconds and longer. The two best methods for this are Time Correlated Single Photon Counting (TCSPC), and Phase and Modulation (Frequency-Domain). HORIBA Jobin Yvon is in the unrivalled position of offering the highest performing instruments of both methods. Frequency-Domain relies on the response of a material to a beam of light that is modulated sinusoidally at high frequency while a PMT provides an electronic signal revealing the change in both the phase and modulated amplitude of the sinusoidal fluorescence emission relative to the excitation beam (fig 1a). This measurement is repeated one after another, at several modulation frequencies to reveal the lifetime of the fluorescent event (fig 1b). However, the sequential nature of these acquisitions requires many minutes to complete an experiment. Clearly, an opportunity existed to improve this approach.

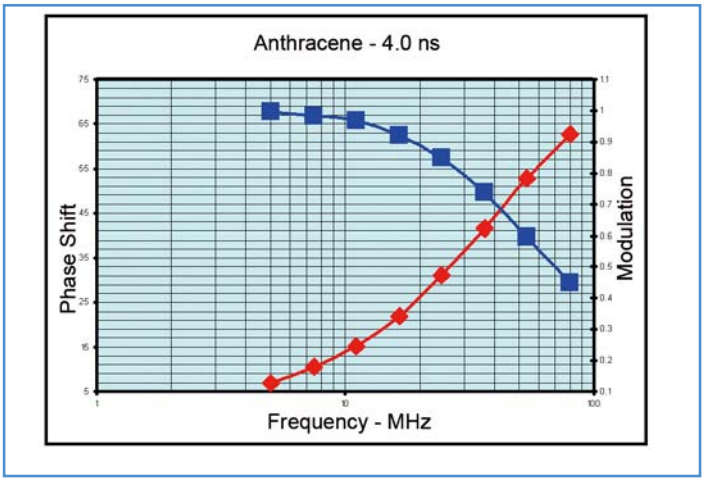


Figure 1b: Fluorescence lifetime of anthracene using eight modulation frequencies from 5 - 80 MHz. The Fourier transform of the sinusoidal modulated fluorescence provided the phase (red) and modulation (blue) data and was analyzed by non-linear least squares fitting. The acquisition time was 4 min by conventional methods. The same experiment on the new MF² instrument required only 0.1s.

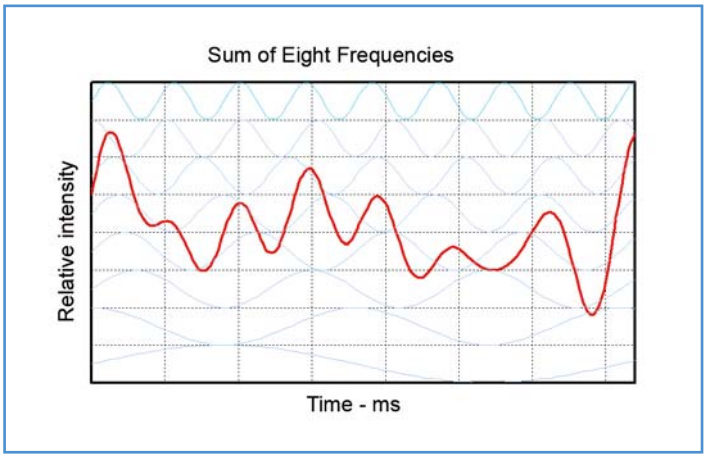


Figure 2: Fluorescence signal elicited from a modulated excitation beam comprised of eight frequencies mixed together. The newly released MF² uses this type of excitation to characterize fluorescence lifetimes in under 10 milliseconds.

We found that recent advances in frequency synthesis allowed us to develop wholly new technologies to bypass limitations of the earlier designs. By grouping multiple frequencies into one high frequency waveform and greatly expanding the available frequency range we decreased the time it takes to measure a fluorescence lifetime from minutes to millisecond, a 10,000 fold change (fig 2). We call this revolution in instrumentation the MF², which delivers previously unavailable experimental speed and performance.

For further information check out our website or contact your nearest HORIBA Jobin Yvon office.

New 265 nm NanoLED reveals rotamers in phenylalanine

David Birch
Head of Department of Physics, Strathclyde University &
Vice Chairman HORIBA Jobin Yvon IBH, UK

Recent research by the HORIBA Jobin Yvon IBH team in collaboration with my Photophysics group in the Department of Physics at Strathclyde University in Glasgow has led to a breakthrough in exciting protein intrinsic fluorescence using AlGaN light-emitting diodes (LEDs). There are thought to be nearly 100,000 proteins in the human body; each one with a unique conformation carefully matched to fulfilling a unique task, but how proteins fold correctly to obtain such unique conformations remains one of the grand challenges of our age. Fluorescence lifetime techniques are among the main methods available for resolving intramolecular structural changes and fortunately nature has provided us with naturally occurring fluorescent markers in the form of amino acids with which to monitor proteins. There are three fluorescent amino acids found in proteins. These are tryptophan, tyrosine and phenylalanine (Figure 1). Because wavelengths of < 300 nm are required the excitation of amino acid fluorescence has hitherto required the use of bulky, expensive or high maintenance pulsed sources such as synchrotrons, mode-locked lasers or flashlamps. This is particularly true for phenylalanine, which requires the shortest wavelength of all the fluorescent amino acids for excitation, and consequently has been little used for protein research.

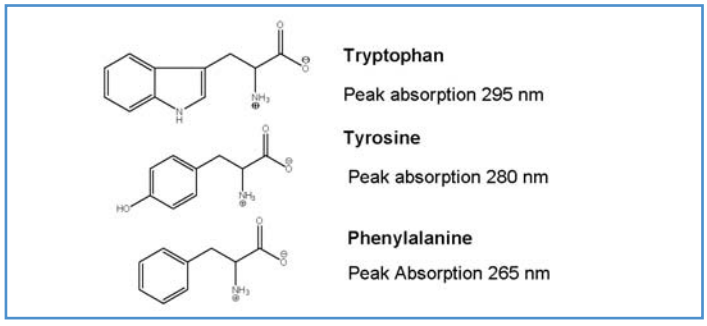


Figure 1. Fluorescent amino acid structure and excitation wavelength. All three wavelengths are now available with the NanoLED

All this has recently changed with our introduction of the latest addition to the successful NanoLED range (Figure 2) in the form of the 265 nm diode, thus complementing LEDs already available for exciting tyrosine and tryptophan at 280 nm and 295 nm respectively.

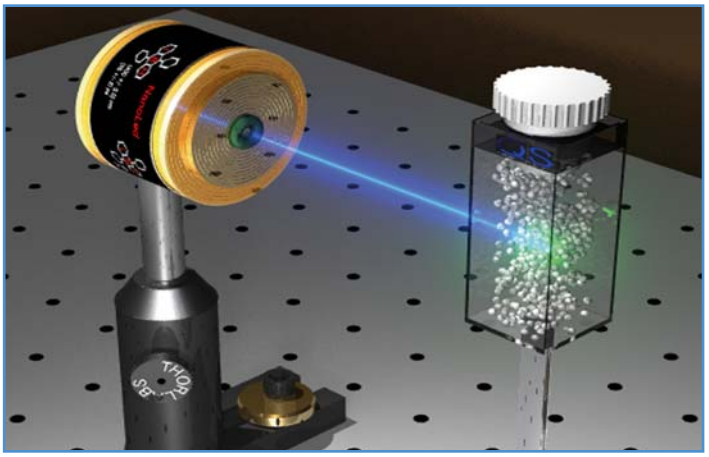


Figure 2: The NanoLED is the size of a table-tennis ball, but as results show, even more adept at displaying dynamics!

In work recently published in Applied Physics Letters Vol 89, page 63901, 2006 we have shown that not only is it now possible to excite phenylalanine fluorescence lifetimes using a low-cost, reliable and easy to use pulsed semiconductor source for the first time, but that phenylalanine has a bi-exponential not mono-exponential fluorescence decay as previously thought (Figure 3). The result is significant for protein research as it means that rotamers caused by preferential orientations of the side-chains shown in Figure 1, and known to exist for tryptophan and tyrosine, also exist in phenylalanine. This has bearing on our understanding of energy transfer from phenylalanine to the other amino acids and paves the way to greater use of phenylalanine as a protein probe.

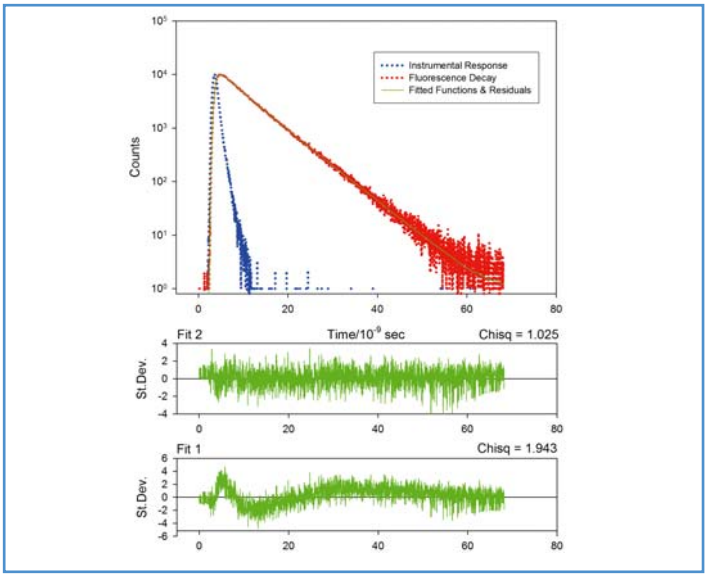


Figure 3: Fluorescence decay of aqueous phenylalanine at 10E-3 mol/l, pH 11 fitted to bi- and mono-exponential functions.

Forensic imaging of gun shot residue using XRF and fluorescence

Simon FitzGerald, Raman and XRF Specialist,
HORIBA Jobin Yvon Ltd, Stanmore, UK

When a bullet is fired from a gun, gun shot residue (GSR) is also discharged from the barrel and other areas of the weapon. GSR is made up of particles from the gun powder (burnt and unburnt), ignition primers and metals (from the cartridge, bullet and metallic coatings). The specific composition of GSR and patterns formed on a material close to the gun (eg, skin or clothing) can provide vital evidence for forensic scientists about the nature of the weapon and its proximity to the material.

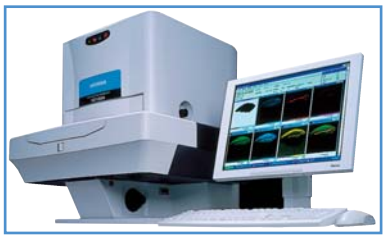


Figure 1: The XGT-5000 x-ray fluorescence micro-analyser

Recent research has investigated the combination of x-ray fluorescence (XRF) micro-analysis and traditional forensic light sources to characterise GSR materials and patterns.

The XGT-5000 micro-XRF analyser provides a facile method for characterising the elemental composition of individual microscopic particles and generating fast element images, with analysis spot sizes down to 10 µm. In addition, a 500W forensic light source (CrimeScope) with short pass filter was used to record fluorescent images from the material, which were digitally captured with the PrintScope.

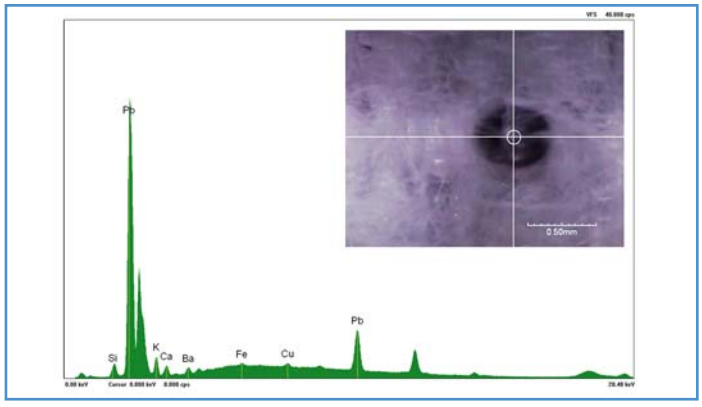


Figure 2: Spot analysis of GSR particle using 100 µm x-ray beam. Inset: white light image showing particle, with analysis region indicated by cross-hairs.

A white light image of a fabric sample held at close proximity to a gun as it was fired, shows a number of dark spots across the sample, whilst the fluorescence image generated using the CrimeScope highlights additional features exhibiting strong yellow fluorescence.

XRF spot analysis of a number of features reveals their elemental composition - in particular, silicon, calcium, potassium, iron, copper, antimony, barium and lead (Figure 2).

Element imaging across the material with 100 µm spatial resolution illustrates the distribution of each element (Figure 3) - in particular, barium and lead containing particles are most concentrated towards the centre of the sample, with barium appearing the most densely located. Calcium and iron containing particles are relatively evenly distributed across the whole sample area. In addition, a small number of copper particles are observed.

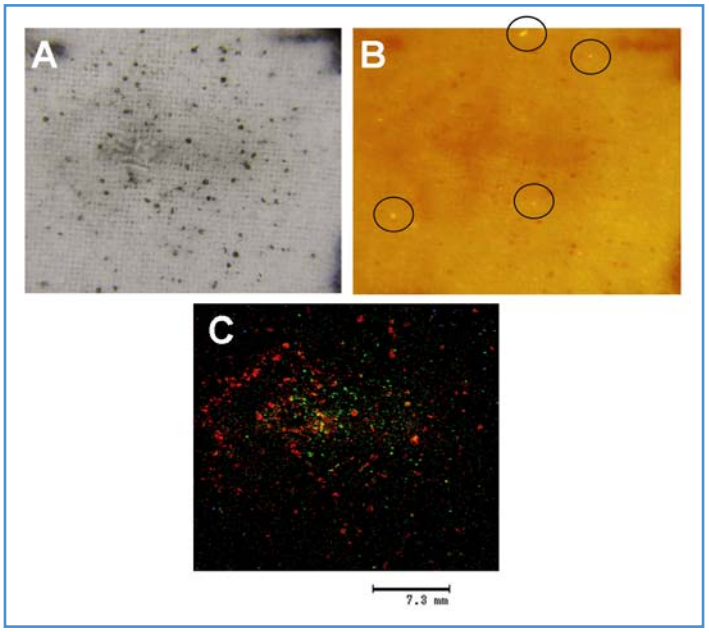


Figure 3: Analysis of gun shot residue on fabric: (A) white light image, (B) fluorescence image with bright spots circled, and (C) composite XRF image showing distribution of lead (red), barium (green) and iron (blue).

With the unique 10 µm beam available on the XGT systems, it is also possible to analyse the individual particles, which range in size from 10-50 µm (for calcium, iron and barium) through to 200-300 µm (for copper).

Further details of this work can be found in the new application note XGTAN-For03 (Gun Shot Residue analysis using X-ray fluorescence micro-analysis), which is available for download from the HORIBA Jobin Yvon website.

Microanalysis website

www.jobinyvon.com/microanalysis

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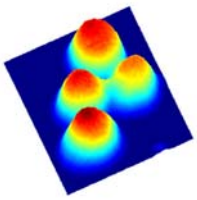
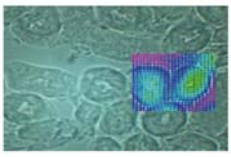


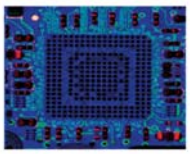
Confocal Raman Microscopy

Raman analysis on the sub-micron scale provides highly detailed molecular information.



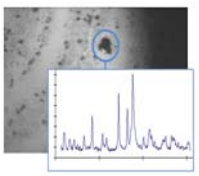
Fluorescence Microscopy

Fluorescence, steady state and time resolved spectroscopic mapping and imaging.



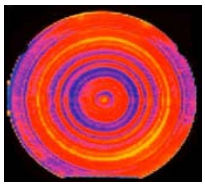
Micro-XRF

Novel monocapillary technology provides access to spatially resolved X-Ray fluorescence analysis down to the 10µm scale.



FTIR Microscopy

Combining both Raman and FTIR microanalysis on the same system.



Micro-PL

High spatial resolution and UV-NIR wavelengths provide important structural, optical and electronic characterisation

FORTHCOMING EXHIBITIONS

25th February - 2nd March 2007
Pittcon
USA

3-7th March 2007
Biophysical Society
USA

25-29th March 2007
ACS Spring Meeting
USA

27-30th March 2007
JSAP Spring Meeting
Japan

10-13th April 2007
FOM 2007
Spain

24-26th April 2007
Interphex
USA

To find out about other conferences and exhibitions at which HORIBA Jobin Yvon shall be present consult our website: www.jobinyvon.com

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