

Raman Microanalysis in Forensic Laboratory

Providing Raman solutions for over 20 years

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Presentation outline

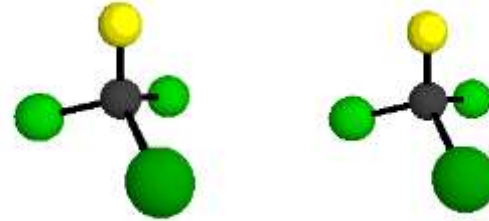
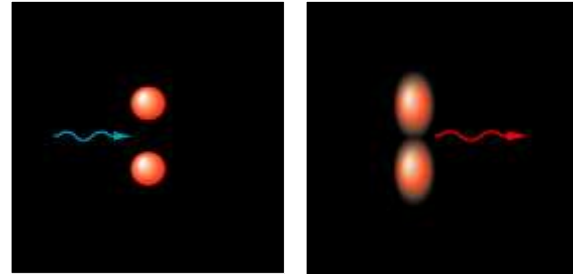
- Raman spectroscopy: what is it and why is it useful in forensics?
- **Renishaw portfolio**
- Examples of the use of Raman spectroscopy in forensics
 - Explosives
 - Drug analysis
 - Questioned documents

Raman spectroscopy

What is it and why is it useful in
forensic science?

What is Raman spectroscopy?

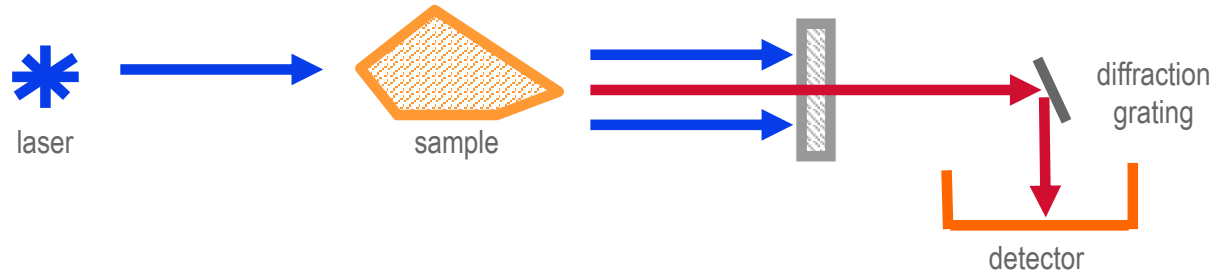
- Light scattering technique
- First reported by Raman in 1928
 - Laser light illuminates the sample
 - Most of the light scatters off without change in energy (elastic)
 - A tiny fraction is inelastically scattered, i.e. Raman scattered
 - This change in energy is specific to the vibrational modes of the molecules
 - The spectrum of this scattered light allows us to identify the sample and better understand its composition



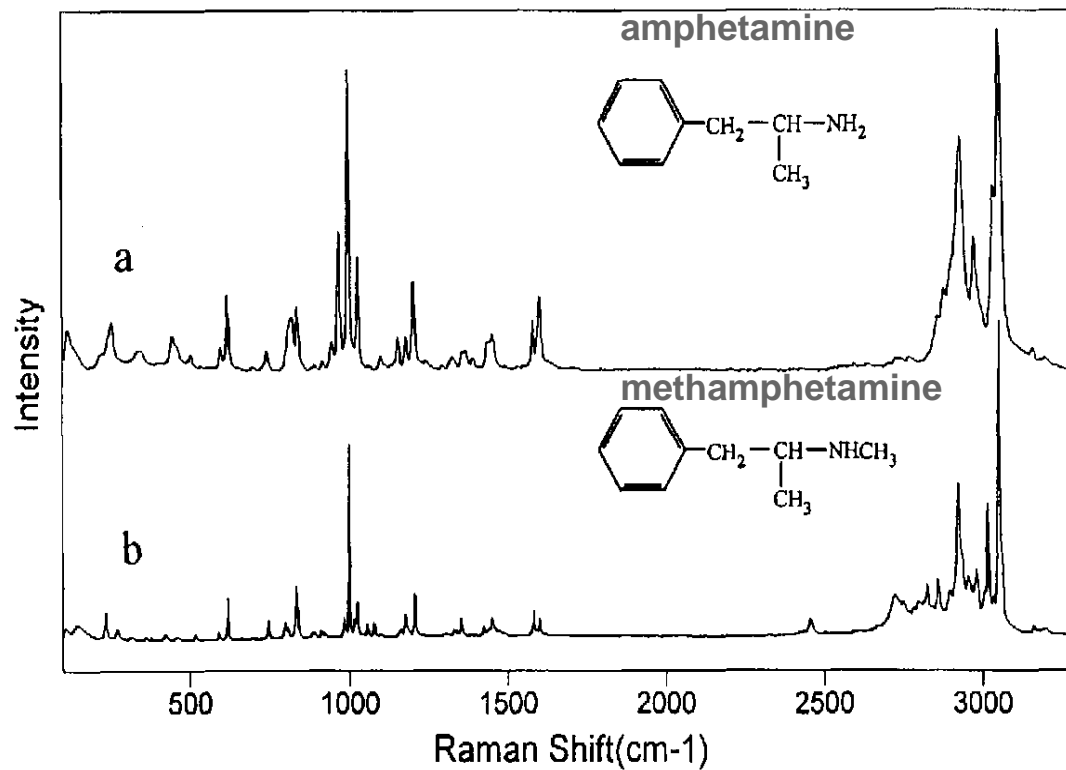
Trichlorofluoromethane

inVia Raman microscope

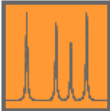
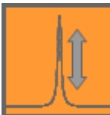
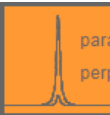


- Main components: laser, microscope, spectrometer
- Laser : excitation light source
- Microscope:
 - Focusing light onto sample
 - Microscope stage moves sample and enables imaging
- Spectrometer:
 - Eliminates the intense Rayleigh and reflected scattered light
 - Disperses the light onto a detector to generate a spectrum



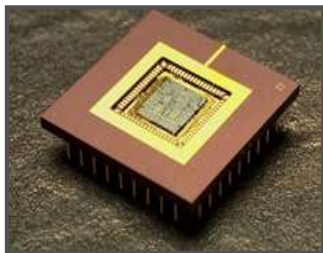
Raman spectroscopy offers high chemical specificity



Information from Raman – Point analysis

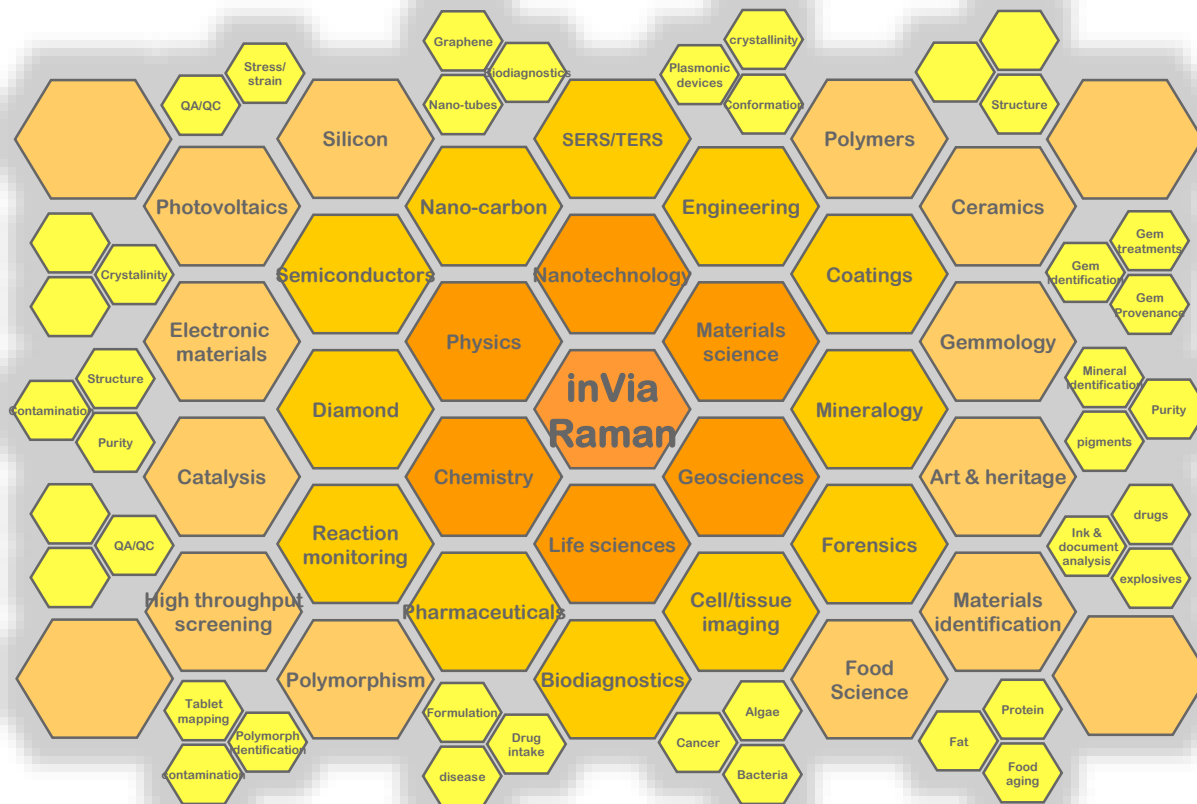
Raman band parameter		Information
	Characteristic frequencies	Chemical and structural identification
	Compare characteristic frequencies	Differentiation
	Variation in absolute / relative intensity	Absolute / relative concentration
 <p>parallel perpendicular</p>	Intensity variation with changing polarisation	Crystallographic orientation
	Variation in band width	Crystallinity
	Variation in band position	Stress / strain state

Advantages of Raman spectroscopy

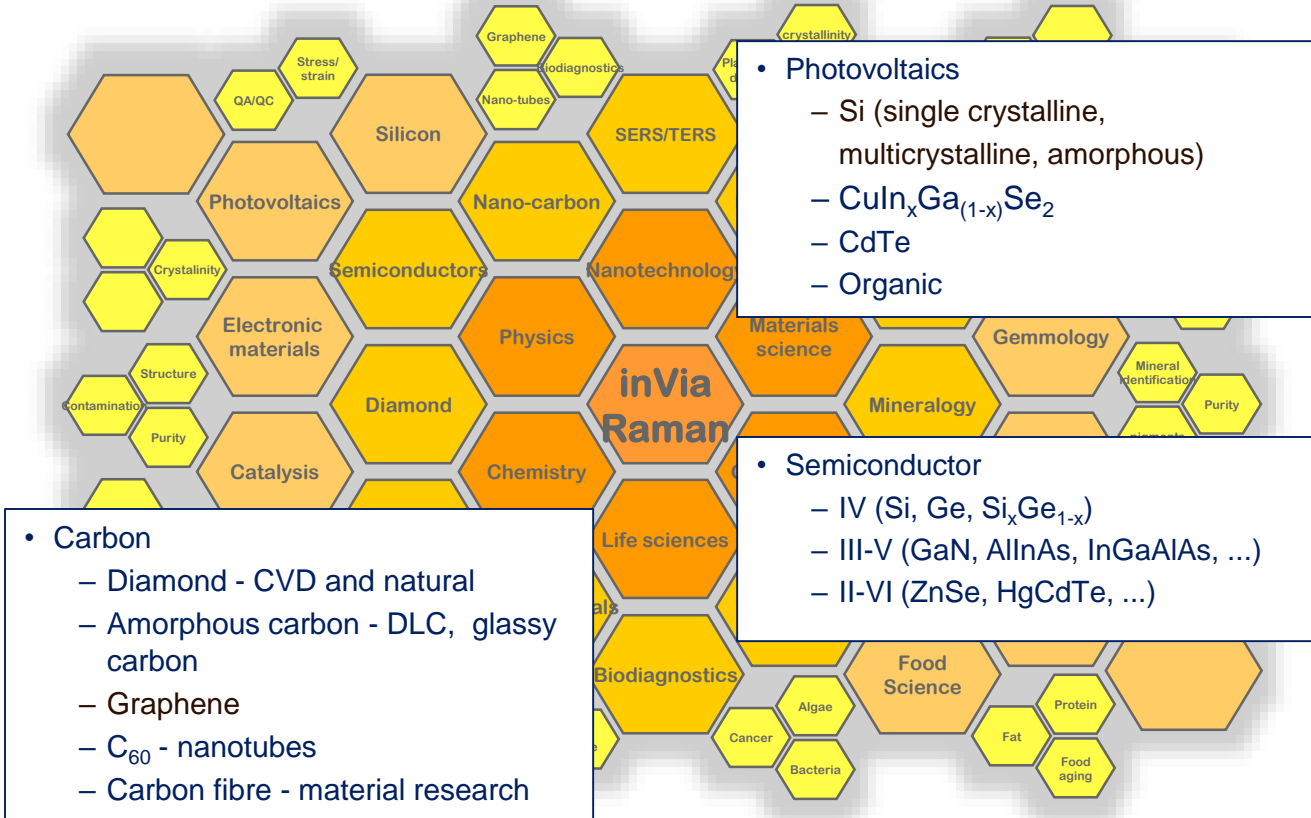


- Non-destructive and non-contact
- Flexible sampling
 - solids, liquids, amorphous,
 - No sample preparation required
 - Fibre probes
- High spatial resolution
 - small (<1 μm) regions can be studied by using a microscope

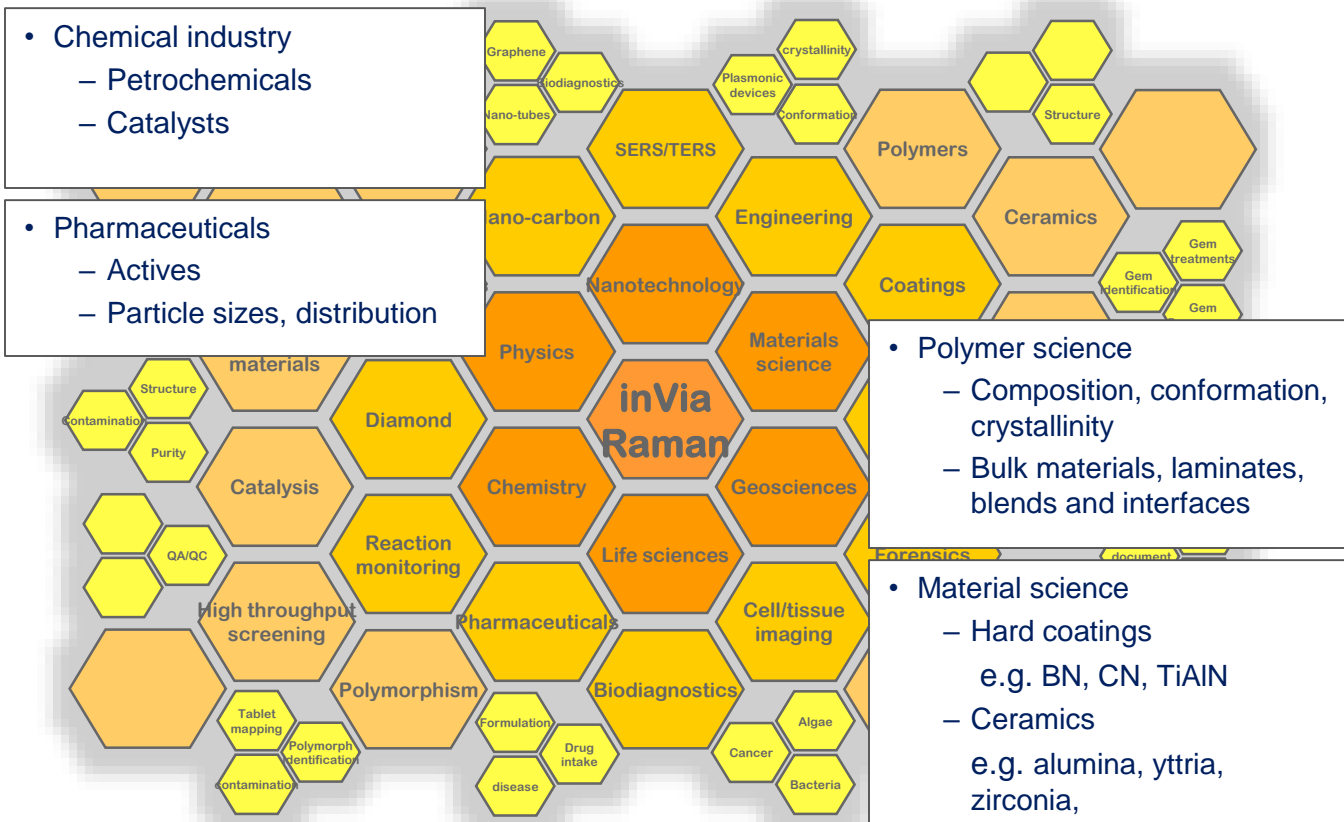
Raman applications



Raman applications



Raman applications



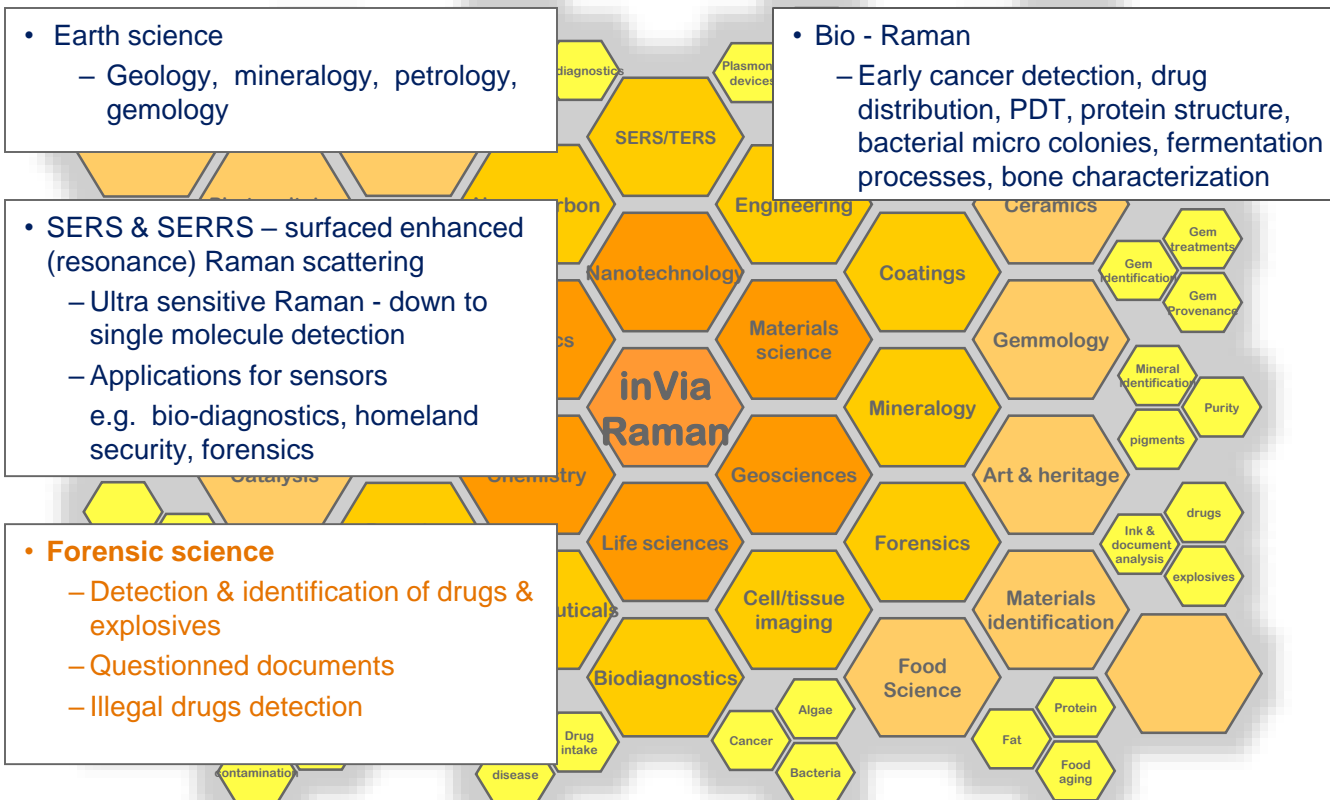
- Chemical industry
 - Petrochemicals
 - Catalysts

- Pharmaceuticals
 - Actives
 - Particle sizes, distribution

- Polymer science
 - Composition, conformation, crystallinity
 - Bulk materials, laminates, blends and interfaces

- Material science
 - Hard coatings
 - e.g. BN, CN, TiAlN
 - Ceramics
 - e.g. alumina, yttria, zirconia,

Raman applications



Renishaw Raman portfolio



inVia Raman microscope –The Raman Swiss knife

- High performance Raman
- Fully automated
- Fully configurable
- Multi-lasers
- Self validation and verification
- Upgrade as your requirements change
- Fully class 1 (option)
- Dedicated forensic libraries



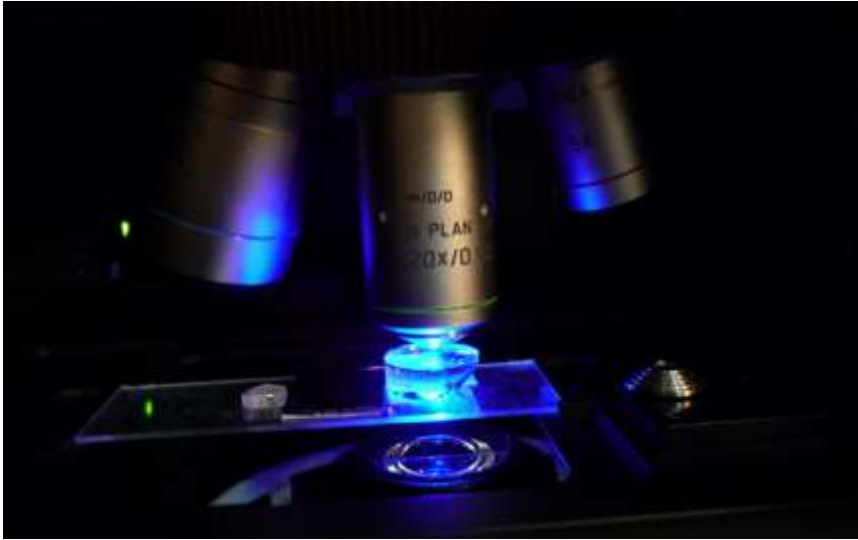
Providing Raman solutions for over 20 years

RA800 series Raman benchtop – Dedicated tool

- Ease of use
- Compact and Robust
- Fast
- Non expert tool
- Fully class 1 (standard)
- Self validation and verification
- One laser
- Dedicated forensic libraries

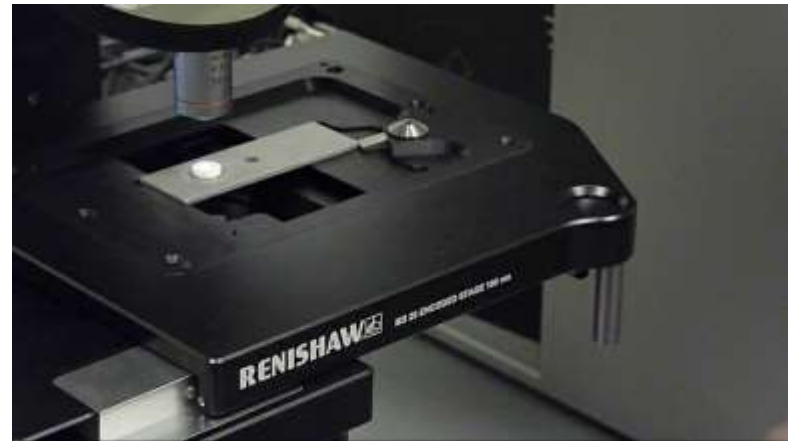
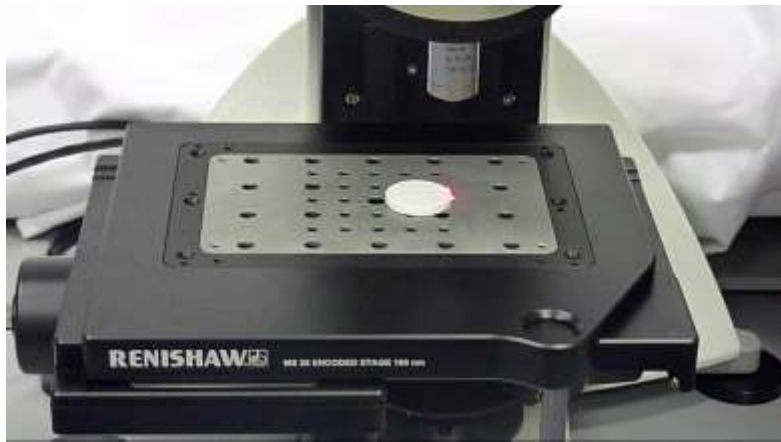


How to use a Raman microscope

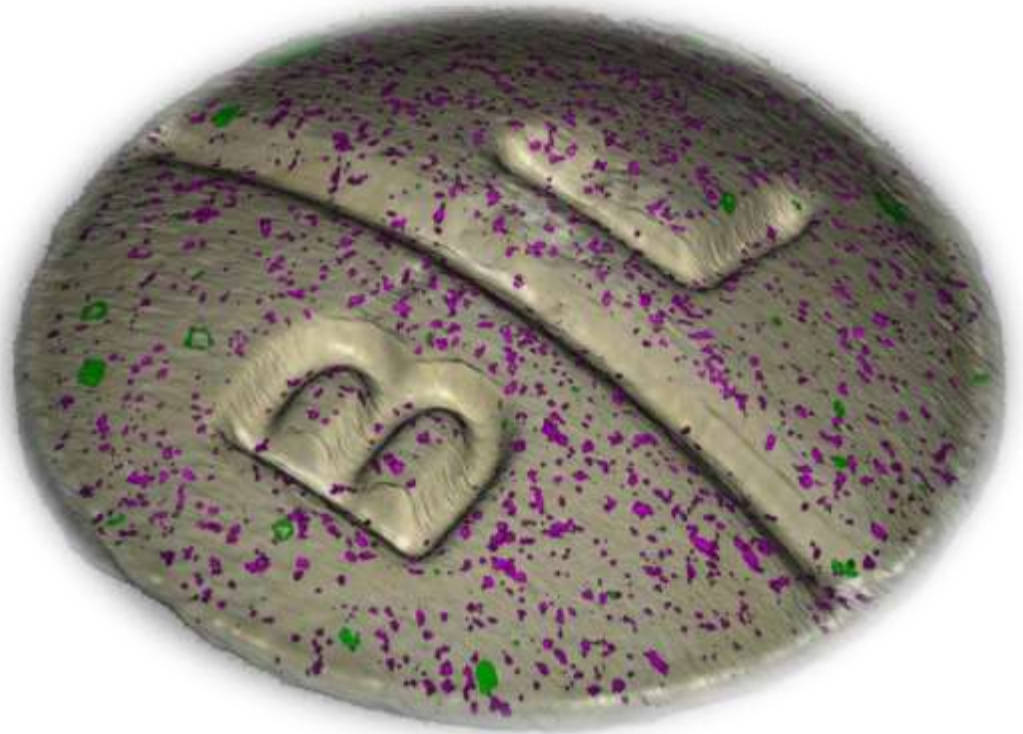
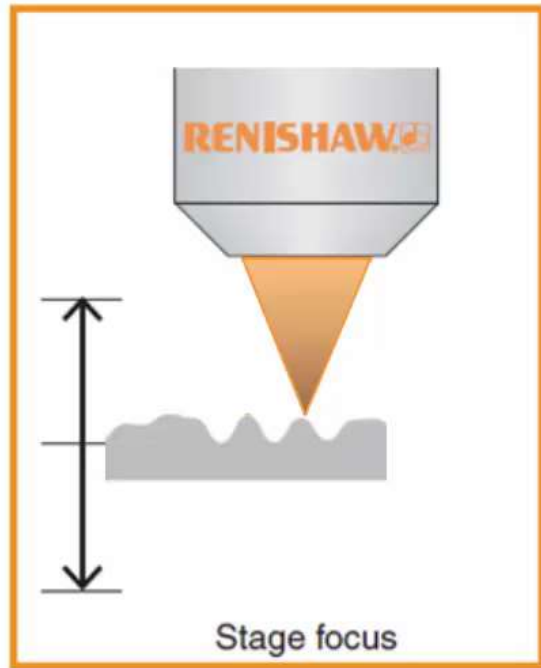


Raman mapping

Renishaw HSES mapping stage – 100nm repeatability



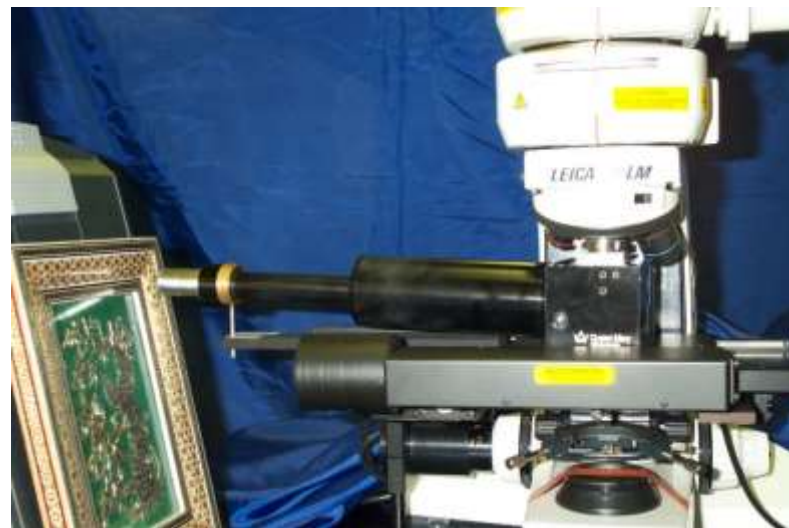
Livetrack - automated real time focus tracking



Flexible sampling -Fibre optic probes



Flexible sampling – large samples



Raman imaging of explosives

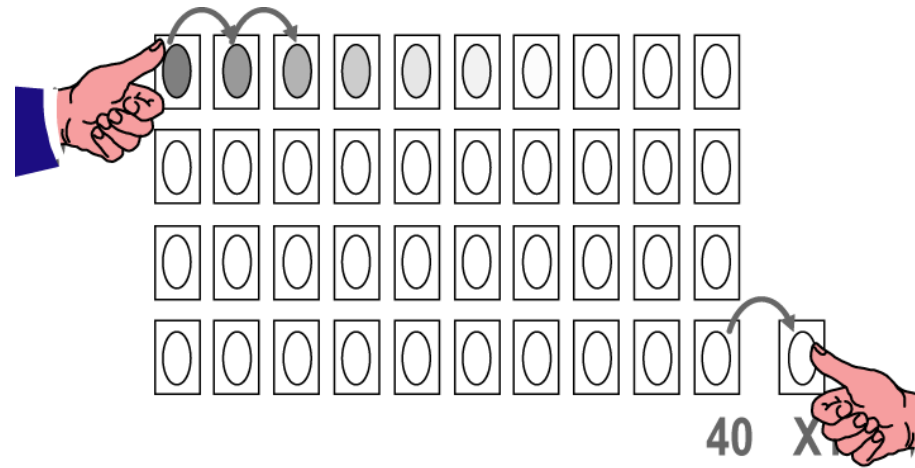


Conventional explosives detection

- Greiss
 - wet chemical
- Sniffers
 - can only sample substances with high vapour pressure
- Gas chromatography
 - transfer of particles to the detector is inefficient
 - technique is **destructive** and slow
- Infrared spectroscopy
 - requires much larger samples than Raman
- Raman spectroscopy?
 - non-destructive and can detect minute amounts of contraband substances
 - detects low vapour pressure substances; potential to identify liquid explosives
 - rapid, highly specific analysis

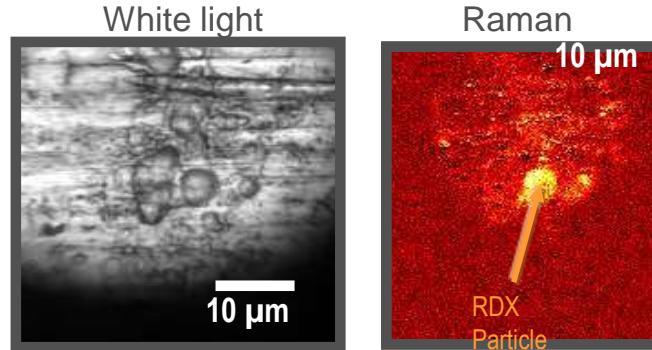
Case study: detecting explosives in fingerprints

- Explosive (Semtex) handled
- Thumb prints applied to 40 aluminum plates in a depletion series (standard Civil Aviation Organization method)
- 2nd generation print made; non-contaminated thumb put on 40th print and transferred to another plate

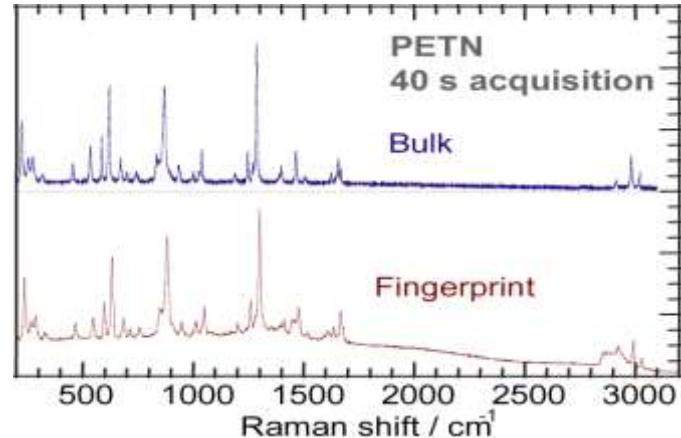


Raman analysis of trace explosives in fingerprints

- White light image locates candidates
- Spectra of particles taken to identify them



Raman spectrum of fingerprint reveals presence of PETN, the explosive component of SEMTEX.

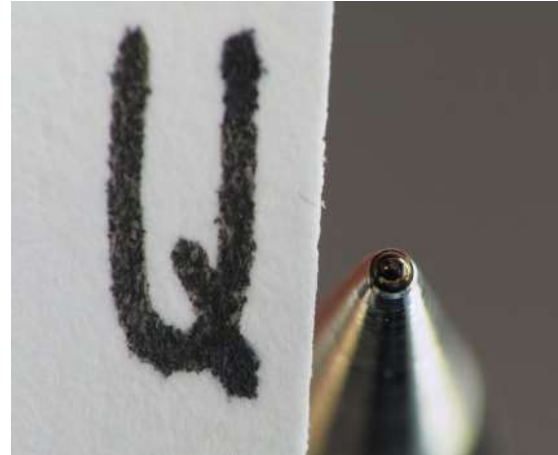


Questioned documents



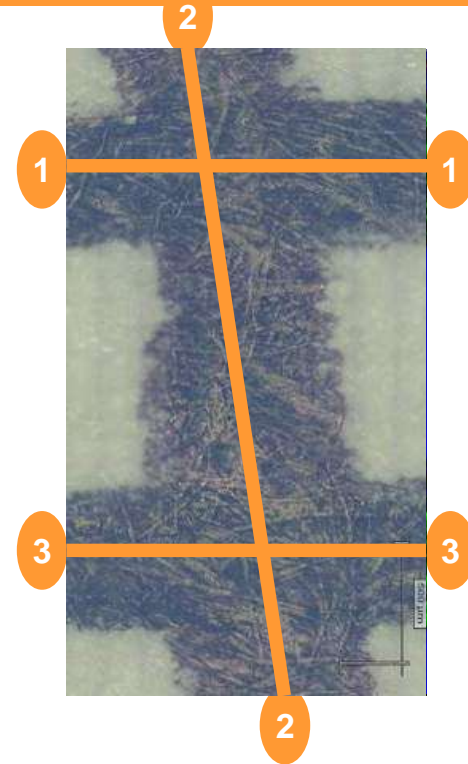
Key issues in fraud cases

- Distinguish inks
 - especially different black inks
- Crossed ink lines
 - which line came first?
- Current techniques
 - optical microscopy
 - fluorescence
 - topographical methods
 - SEM

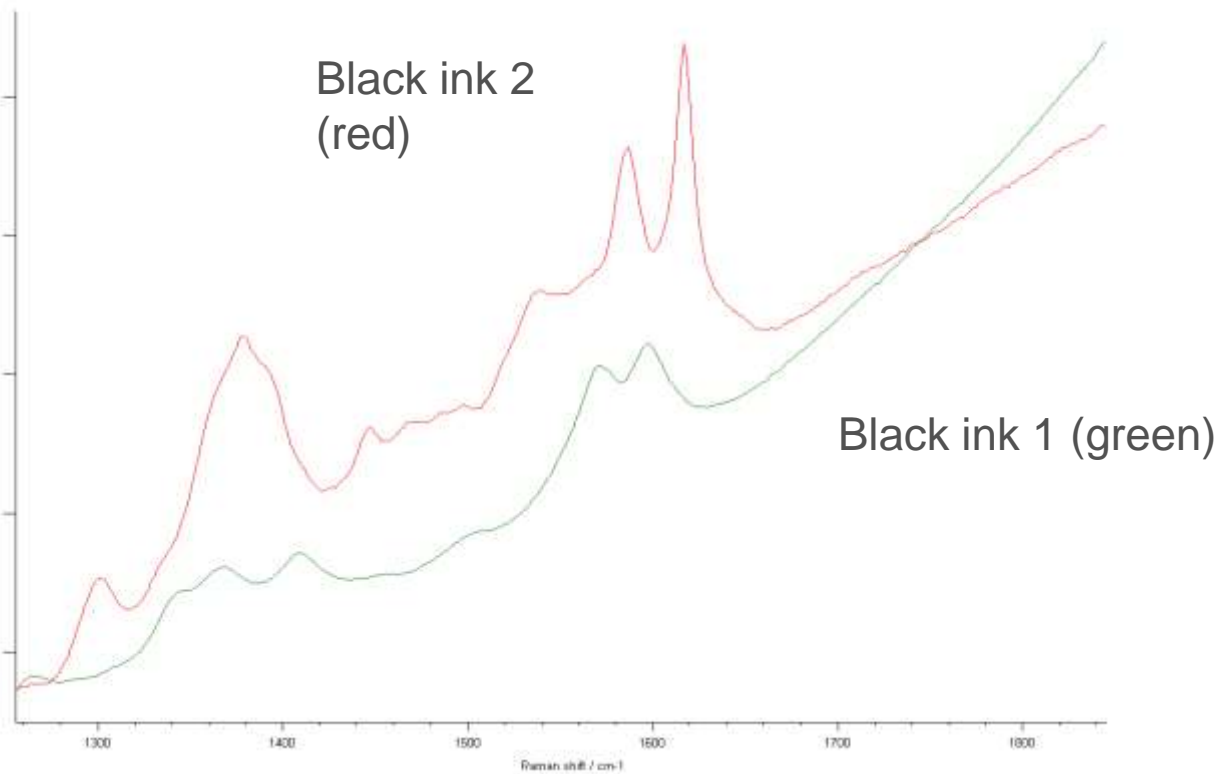


Case study : identifying the sequence of ink deposition

- Double crossed line made with two black ball point pens
- Image of all lines and paper collected in one experiment
 - 1) White light montage
 - 2) Raman image of one ink
 - 3) Overlaid Raman images
- Chemical differentiation of the inks makes it possible to observe clearly the two ink lines crossing



Case study : identifying the sequence of ink deposition



Information from Raman – Mapping

- Raman band parameters can be analysed using two types of methods:
 - Univariate – based on raw data or curve fitting
 - Multivariate – algorithm based i.e. DCLS, PCA, or MCR-ALS
- Information derived from Raman band parameters can be used in conjunction with different dimensions such as time, temperature, distance, area, and volume, e.g.
 - Thickness
(Intensity with depth – 1D)
 - Domain size and distribution
(Intensity with area – 2D / 3D)

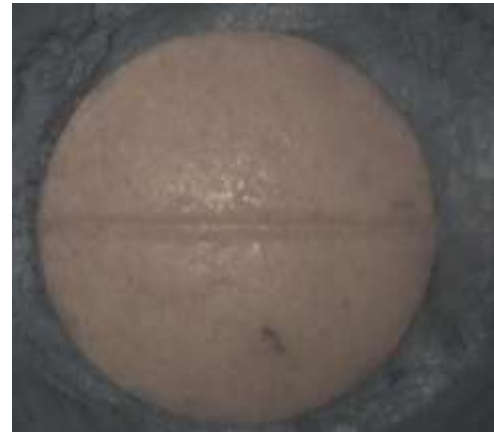
Drug of abuse



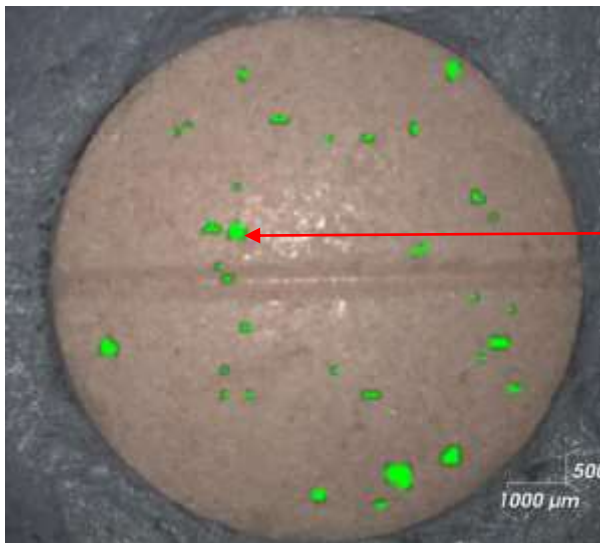
Case study: identifying tablet in its evidence bag



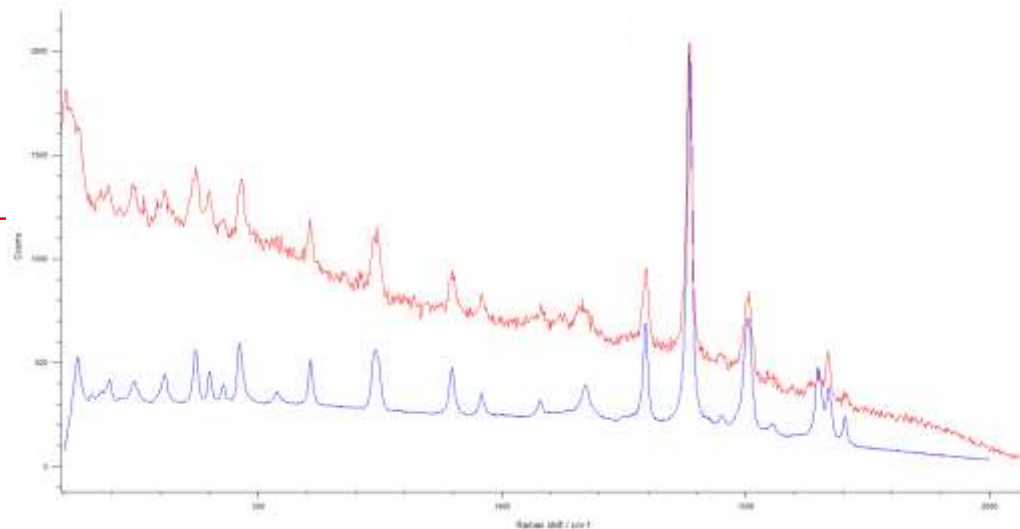
Tablet in evidence bag



White light macro image of
tablet



Macro image of tablet with first chemical component superimposed (green spots)



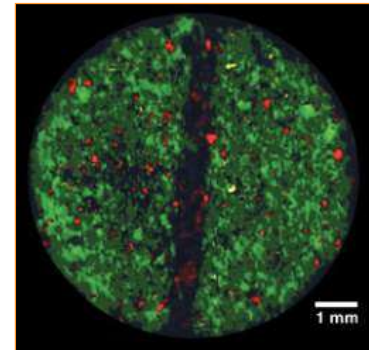
Identification of drug component (red) as amiloride (blue reference)

Case study: identifying tablet from nightclub

- **StreamLine™ Plus image of tablet**
 - Automated analysis of data determines spectra of chemical components
 - Comparison of 'red' component with electronic database identifies it as MDMA ('Ecstasy')
- **Tablet did not require grinding or sectioning**
 - Evidence is preserved
- **Data analysis was performed objectively by the computer**
 - Raman expert was not needed

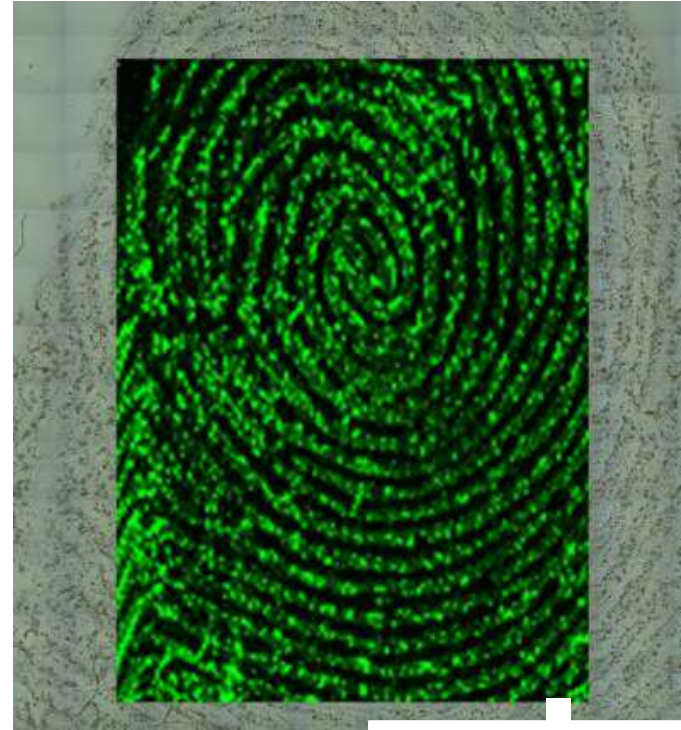


StreamLine™
Plus image of
Ecstasy
Tablet



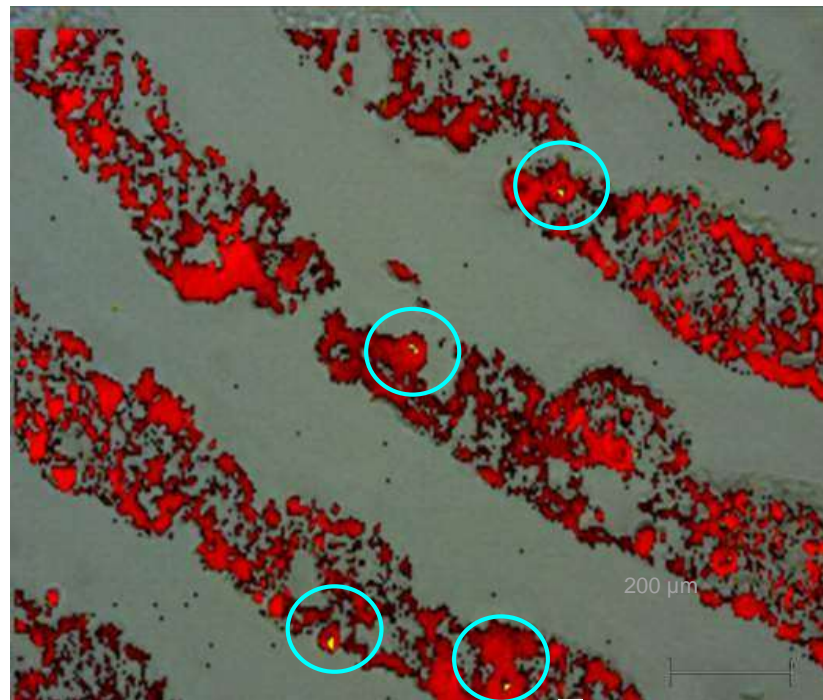
Raman imaging of a fingerprint

- First ever large fingerprint Raman image
- 16,564 spectra
- 12.5 minutes measurement time
- 66 micrometer step size
- 532 nm excitation
- Component analysis (DCLS) multivariate analysis

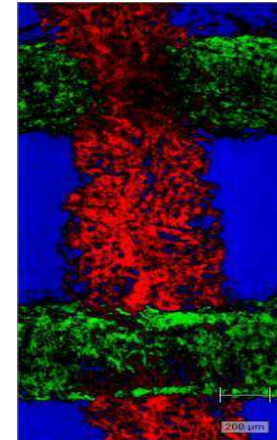


Identifying unknown substances in fingerprint A

- Trace amount of cocaine particles on fingerprint
 - Fingerprint residue in red
 - Cocaine particles in yellow
- High spatial resolution with 5 μm steps
- 532 nm excitation
- 55,020 spectra



Conclusions



Raman spectroscopy and forensics

- Raman spectroscopy provides a valuable and unique insight into the chemical structure of a range of materials
- Raman spectroscopy is having a growing interest in the forensics field
- Renishaw are world leaders in this field, producing a range of high quality instruments that can be custom designed to apply to a number of different forensic applications

Questions ?

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