

Raman Spectroscopy: an aid to forensic and crime scene analysis

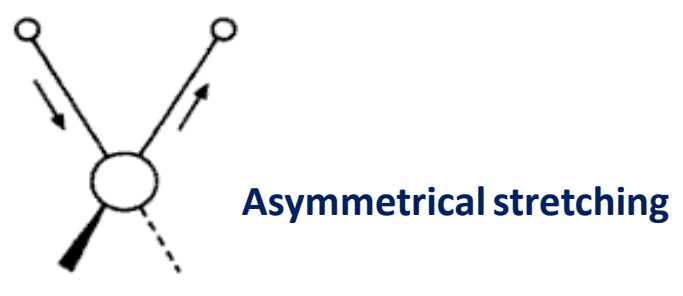
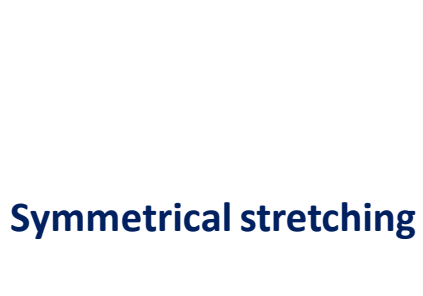
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- **Raman spectroscopy is a vibrational spectroscopic technique used for structural elucidation of materials.**
- **Raman spectroscopy probes the vibrational modes of the target molecules. These vibrational modes can be regarded as a fingerprint that uniquely identifies the substance. It provide information on the chemical structures and physical characteristics of materials .**
- **Unique vibrational signature of the material**
- **Quantitative analysis.**

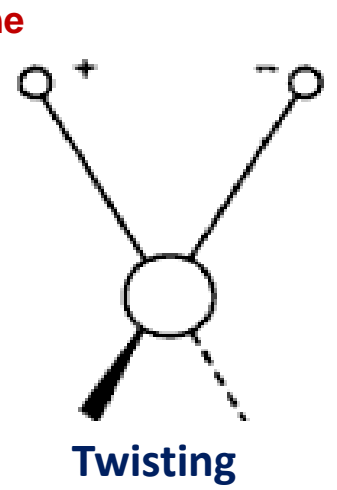
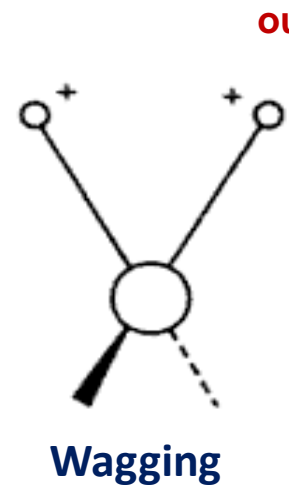
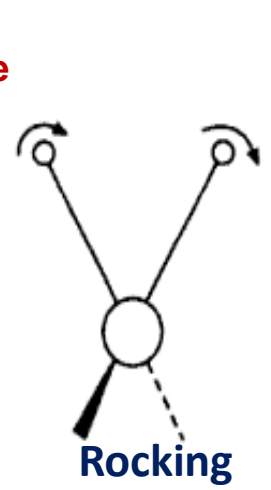
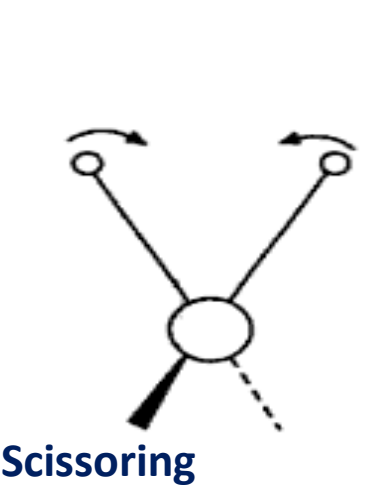
Molecular vibrations

- Raman spectra results from transitions between quantized vibrational energy states.
- Molecular vibrations range from simple motion of two atoms of a diatomic molecule to more complex motion of every atom in a large polyatomic molecule.

A- Stretch: Vibrations along the line of the bond

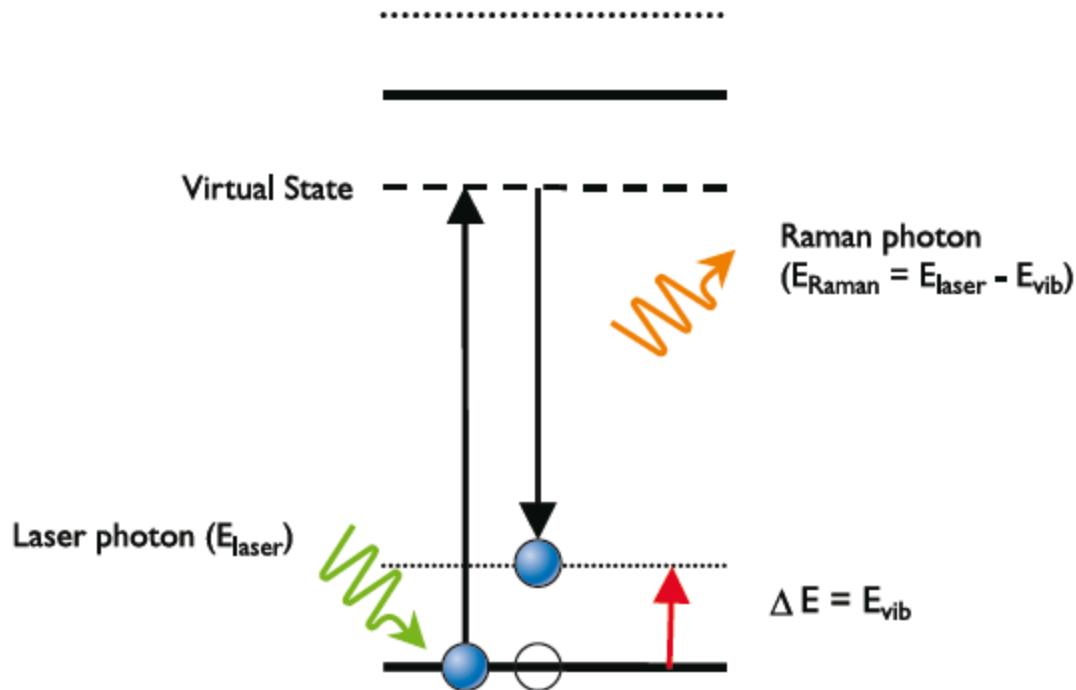


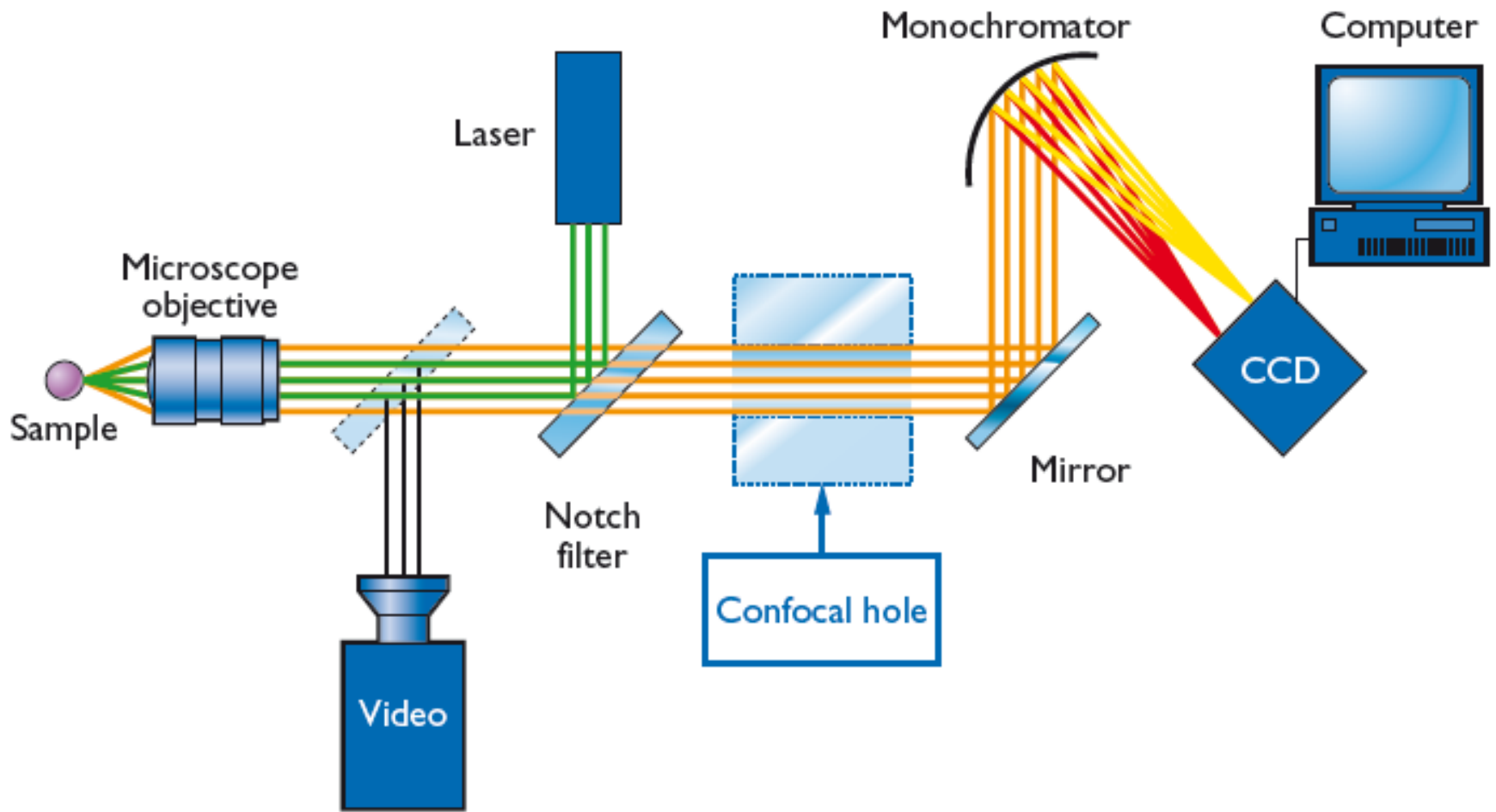
B- Bend: Vibrations not along the line of the bond



🌟 The Quantum theory of Raman scattering

- When a material is illuminated, light will be scattered, reflected or transmitted. A very small part (1 in every 10^7 photons) is scattered inelastically Raman scatter.
- A laser photon excites material to a state with a very limited lifetime (virtual state). When the material returns to its ground state, it loses a well-defined amount of energy to a vibration in the material. The remaining energy, i.e. the difference between the energy of the laser light and the energy involved in the vibration, is released in the form of a Raman photon.





Schematic representation of a dispersive Raman spectrometer

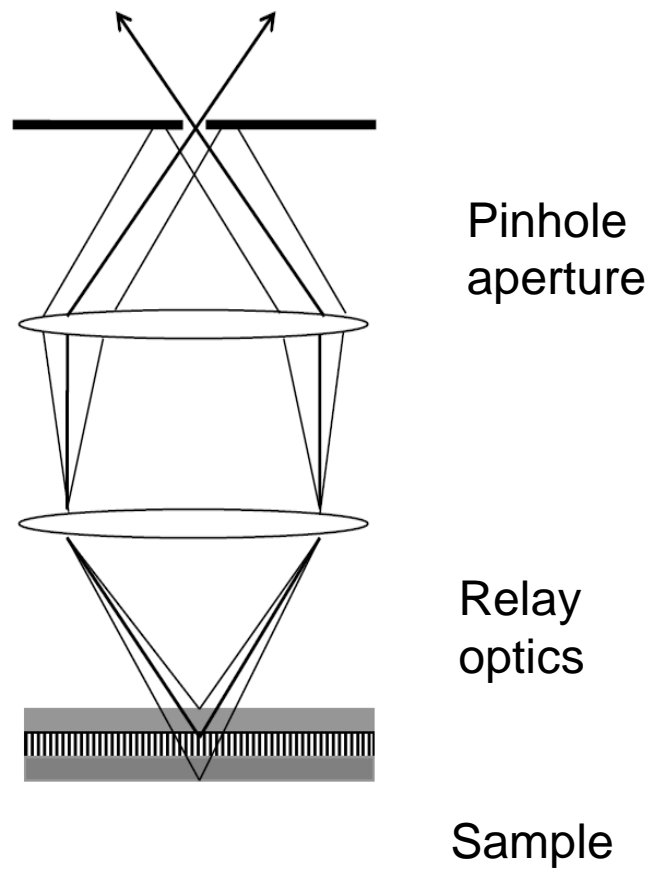
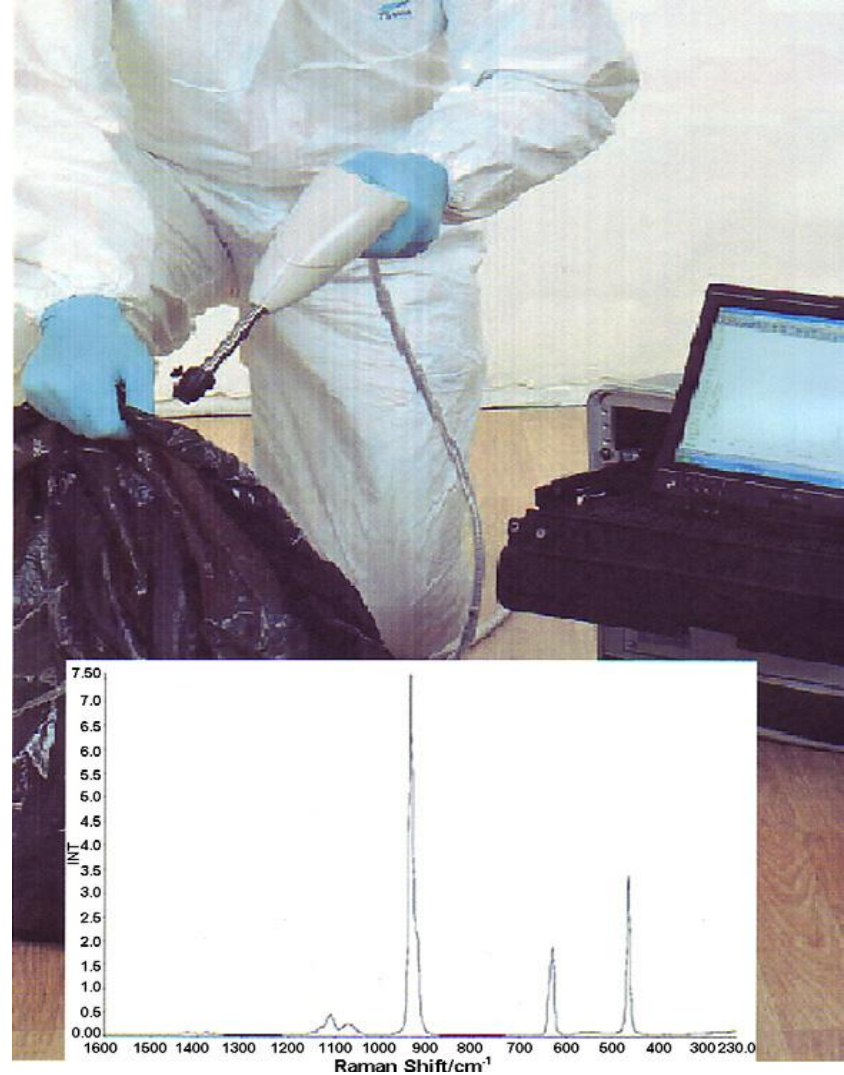
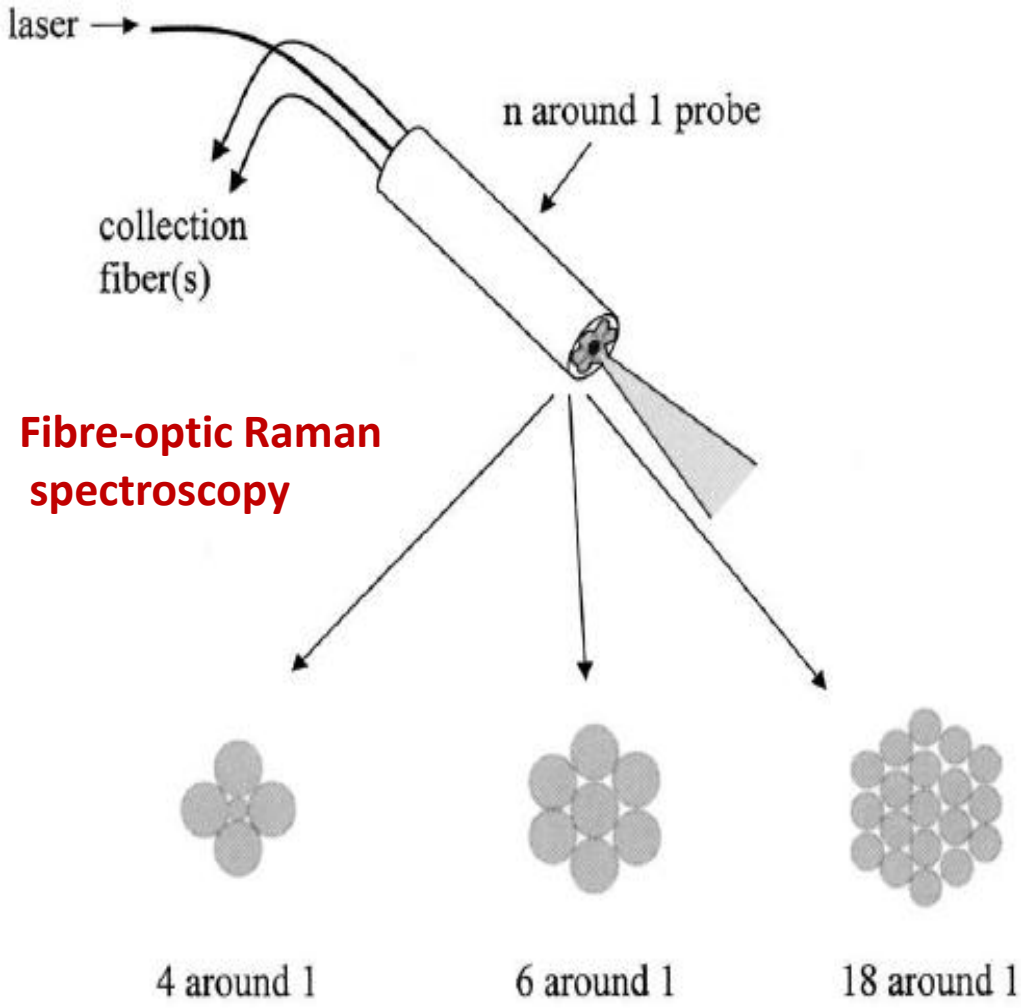


Diagram for a confocal Raman set-up

- *Analysis of microsamples: Only light from a specific depth in the sample is transmitted through this small hole .*
- *Spatial resolution of up to 1 μm :confocal optics exclude Raman signal from regions outside of laser focal cylinder .*
- *Chemical imaging using a motorized stage :depth-profiling and x–y mapping to produce 3D images*

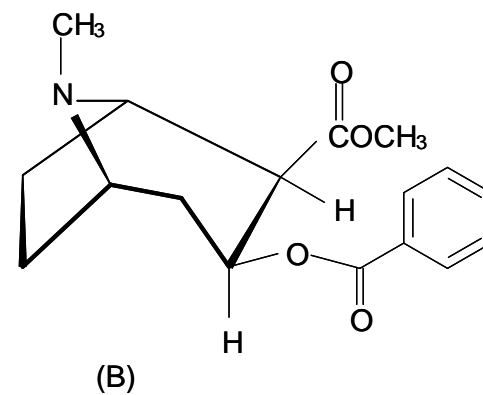
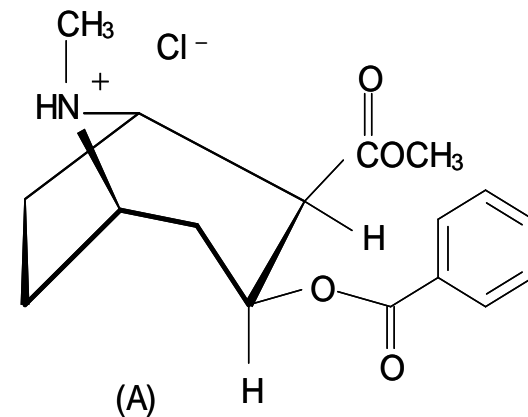
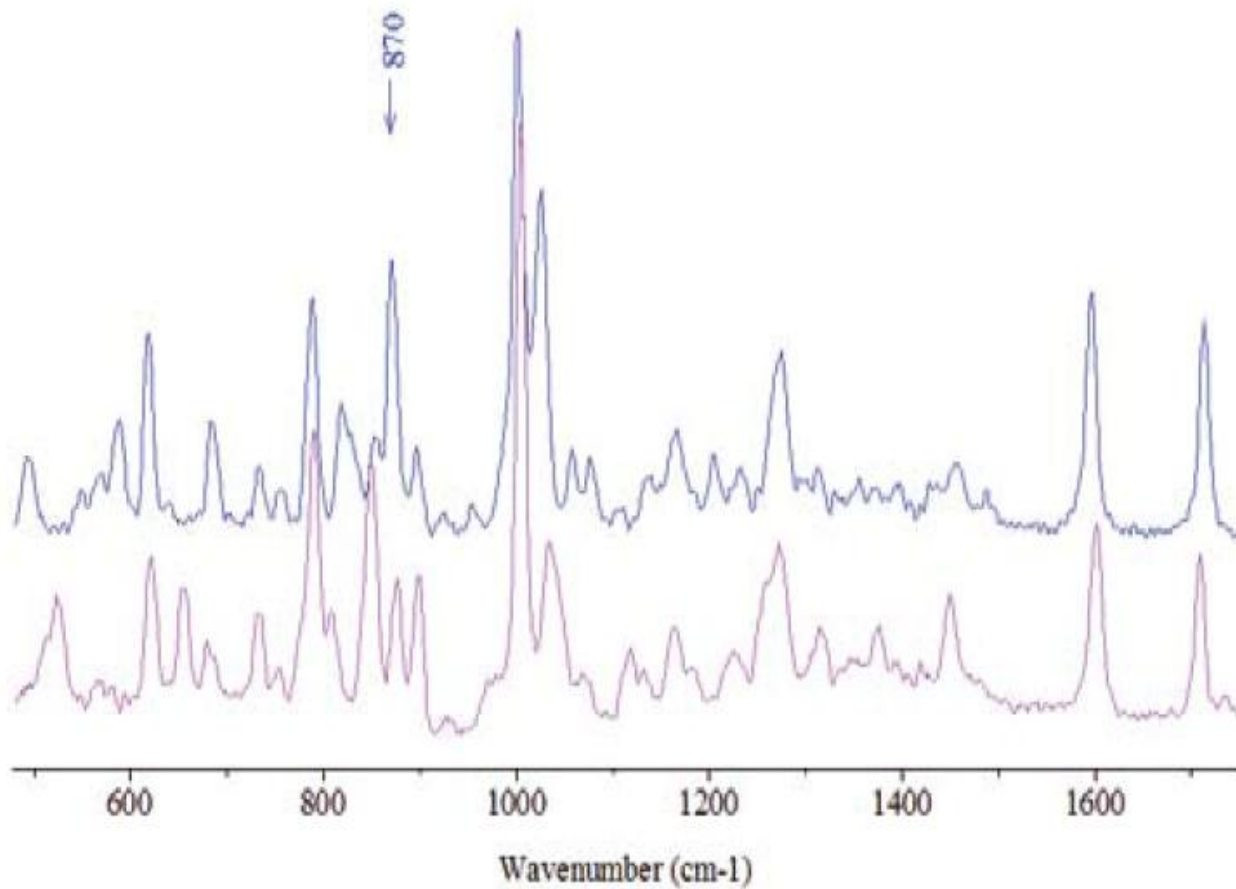


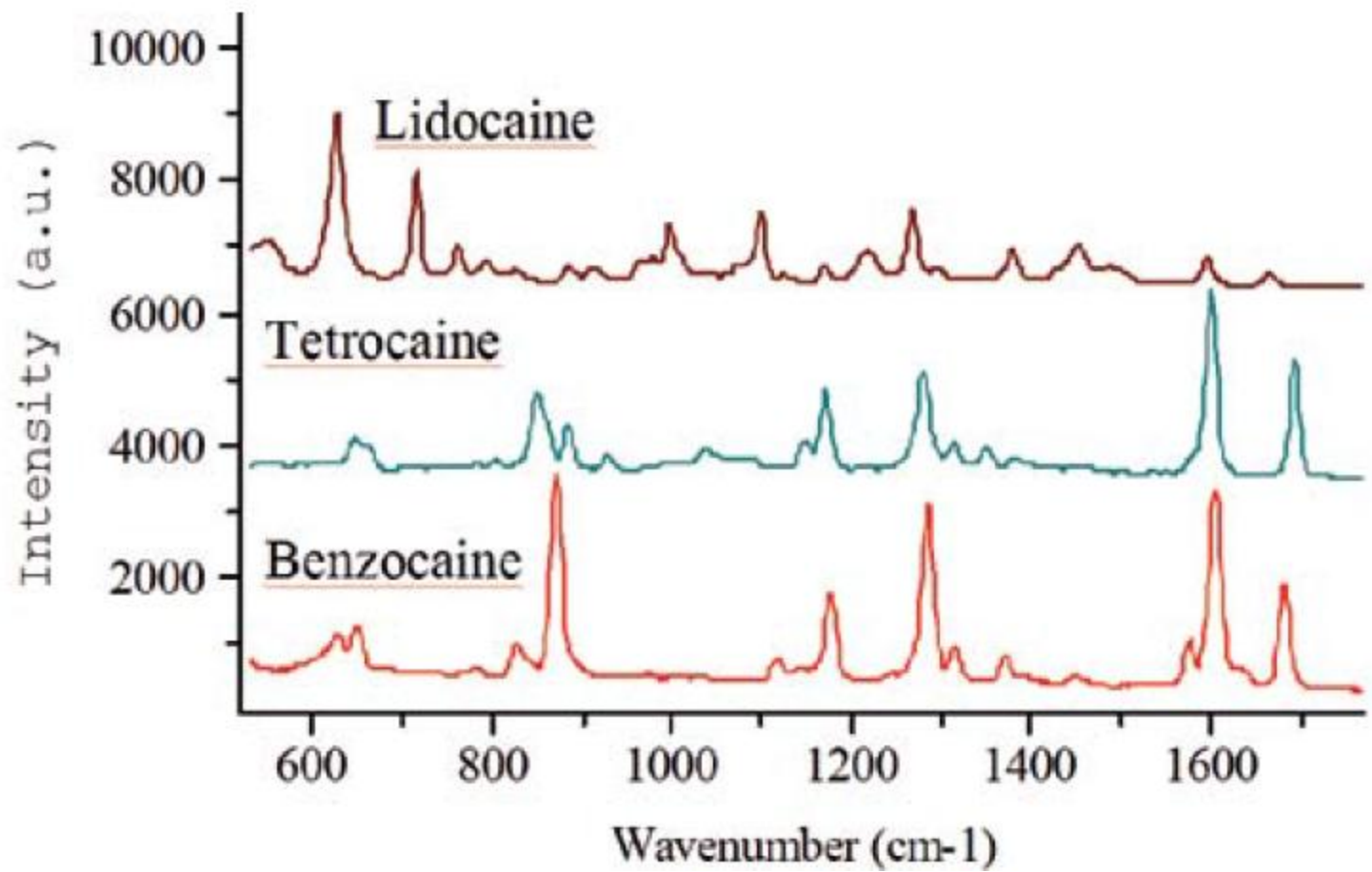
● Portable Raman instruments equipped with remote sampling probes made it easy to analyse a wide range of sample types at the scene in few seconds.

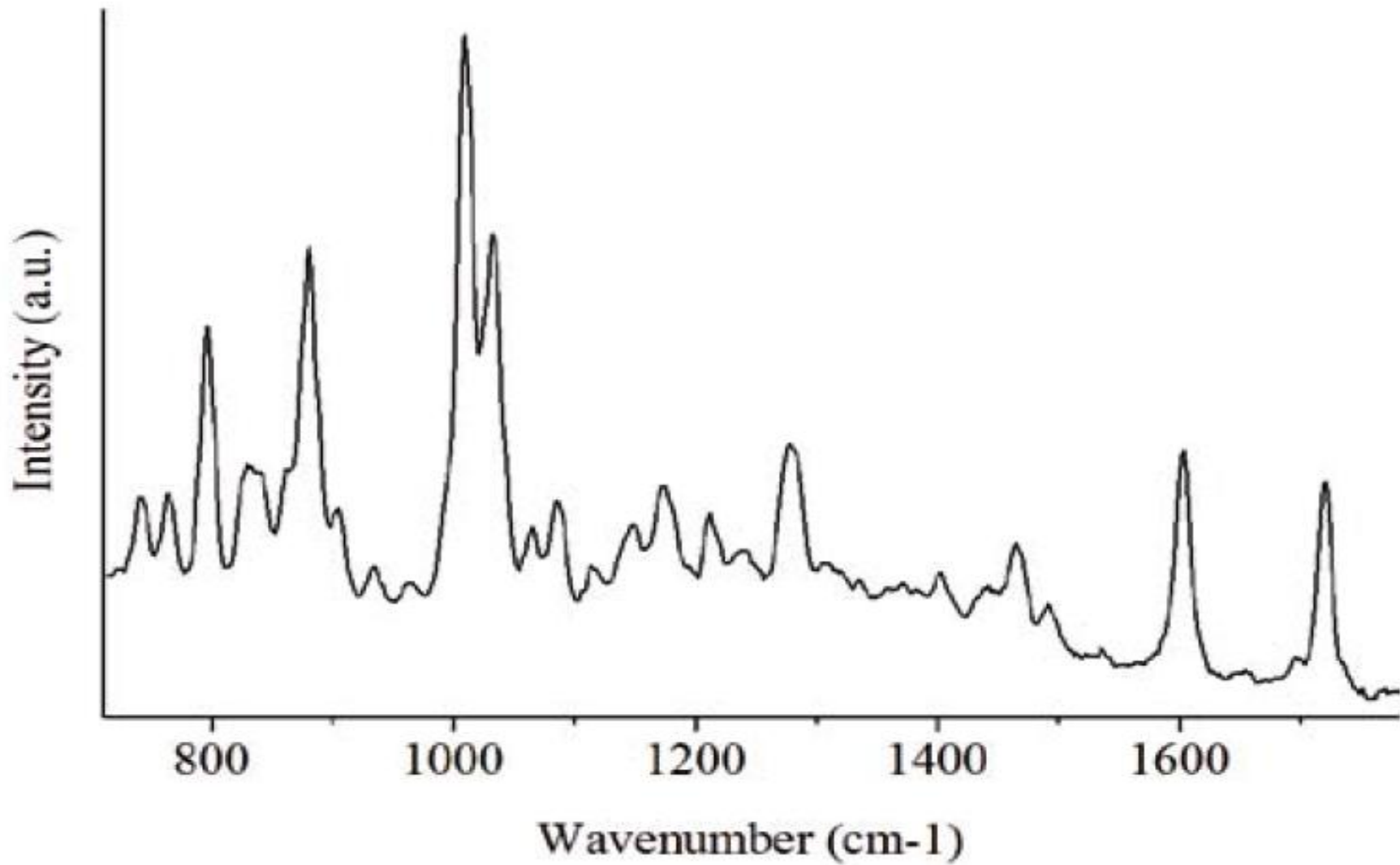
● Spectral libraries and chemometric software are now capable of carrying out in-field investigations

Applications of Raman Spectroscopy in Forensic Science

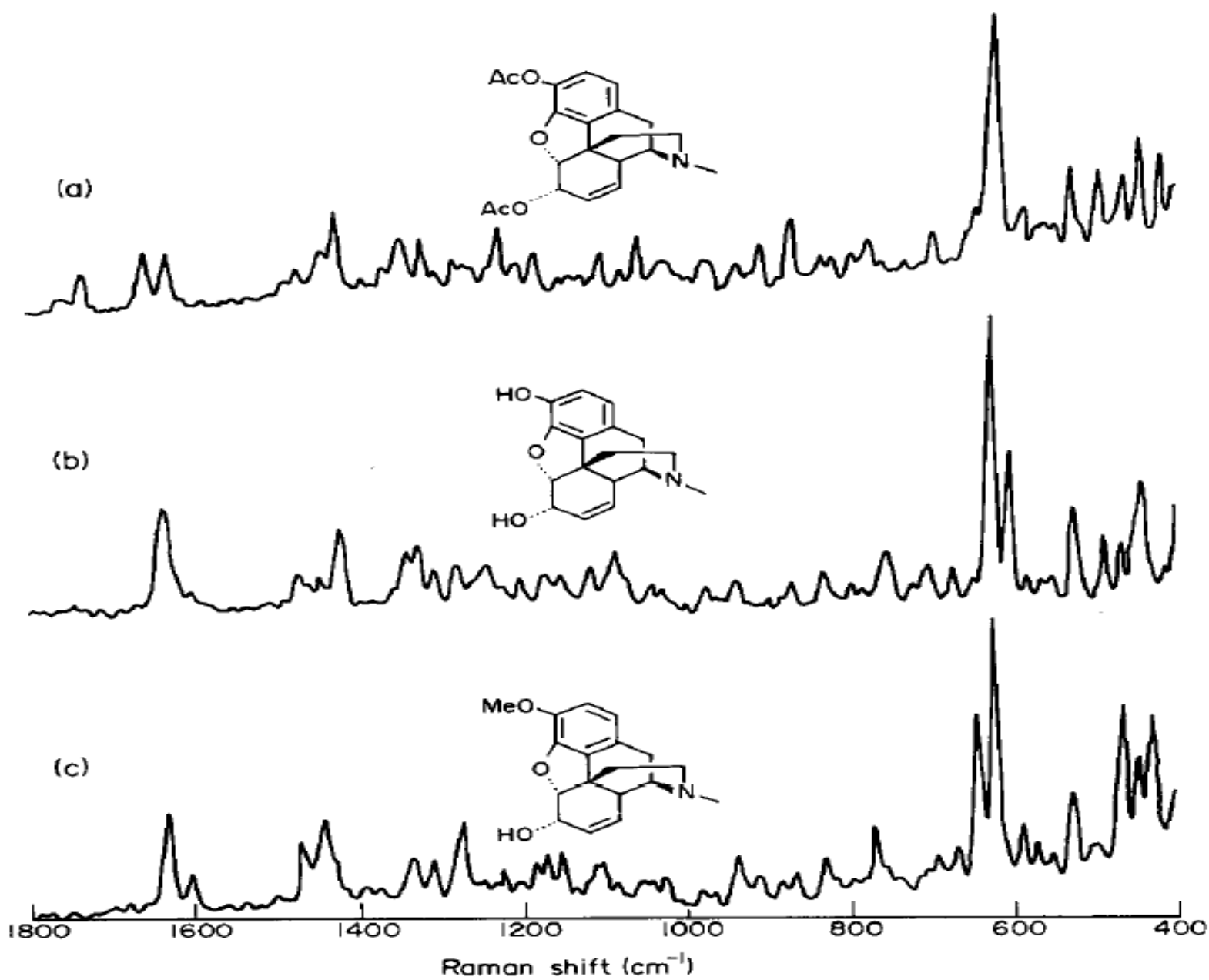
I- Drugs of Abuse







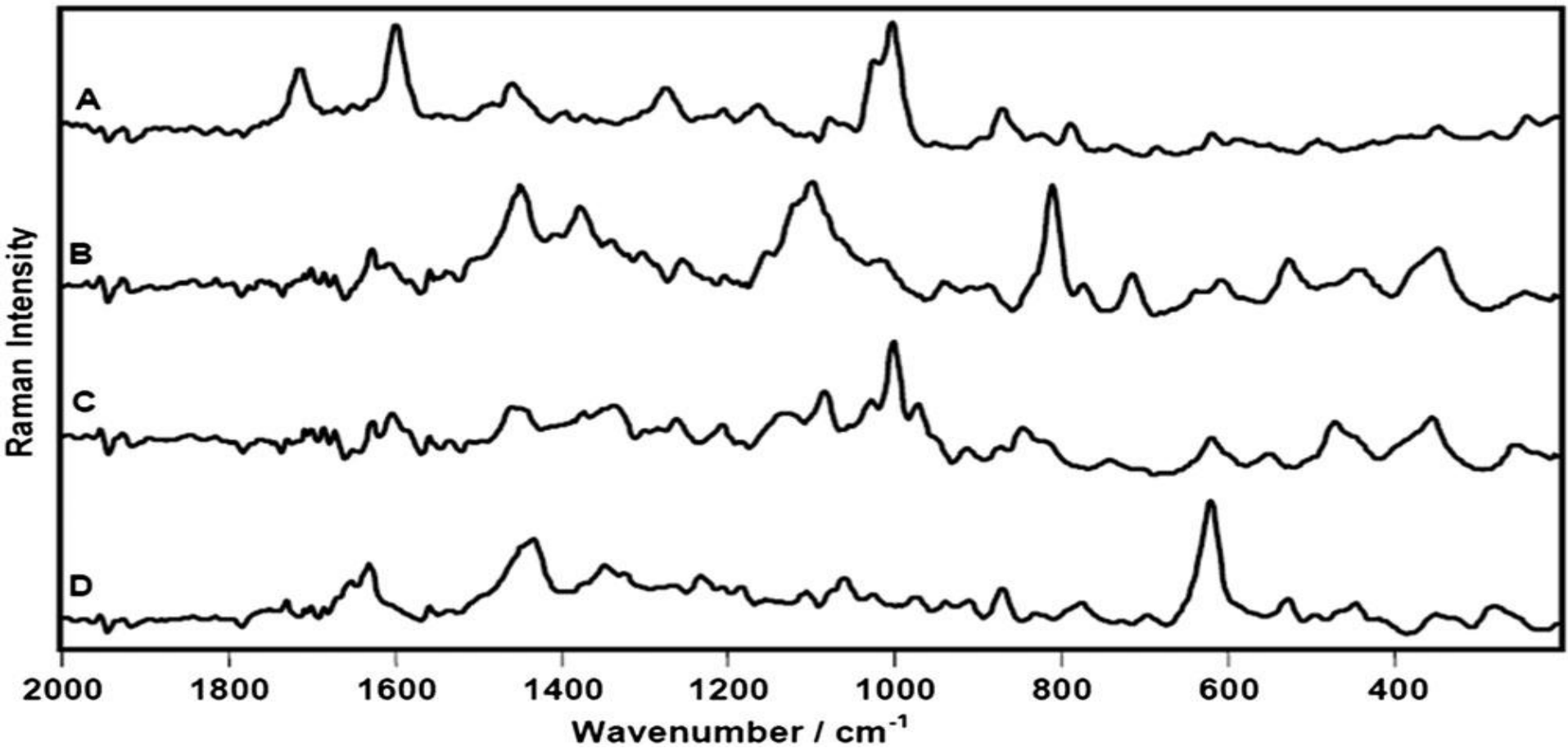
Cocaine + Manitol (50:50)%W - Manitol



a:heroin

b:morphine

c:codeine



Raman spectra of seized drugs of abuse inside plastic bags.

A: Cocaine hydrochloride.

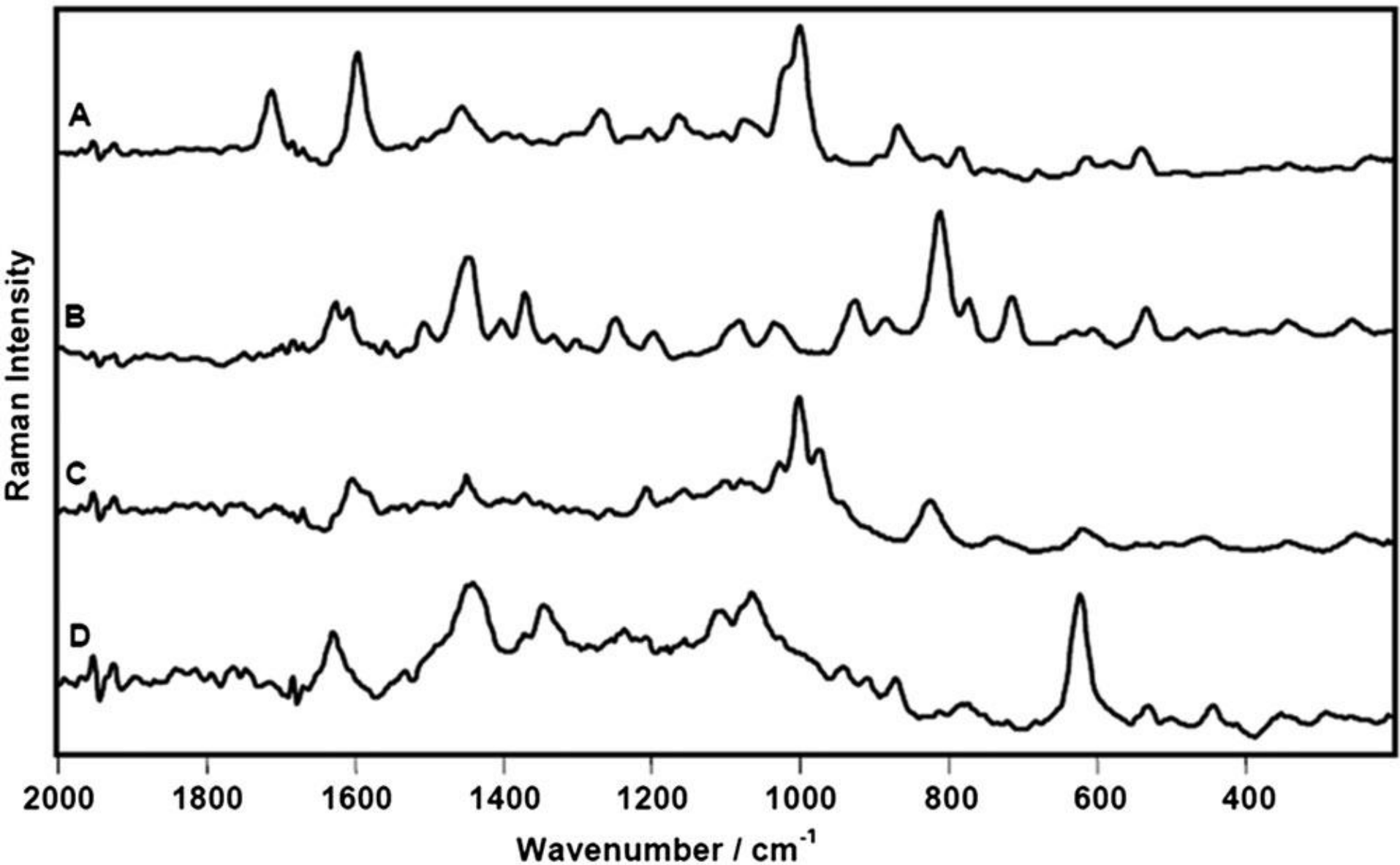
B: MDMA tablet.

C: Amphetamine.

D: Heroin.

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Raman spectra of drugs of abuse inside green glass containers.

A: Cocaine.HCl

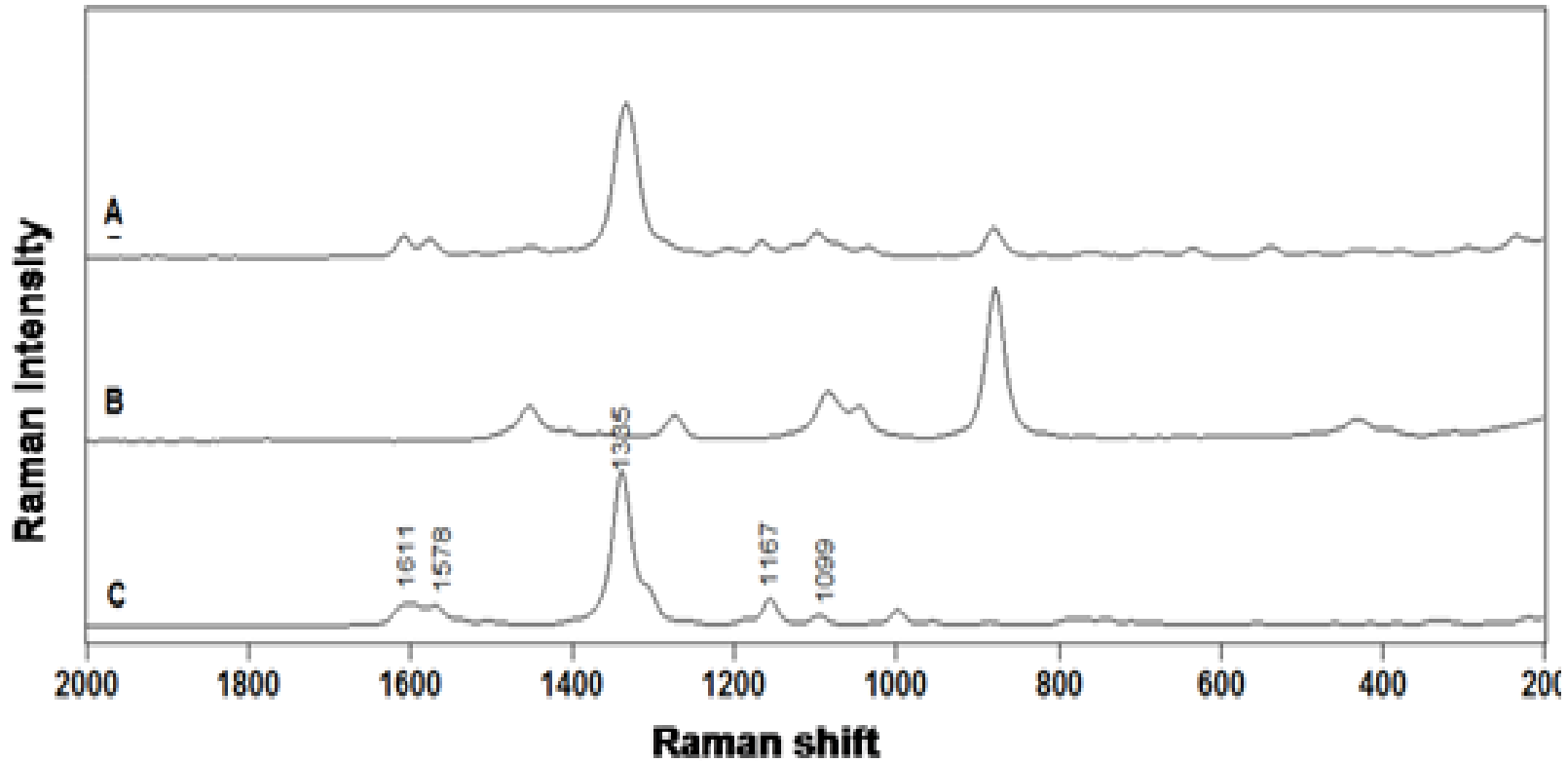
B: MDMA.

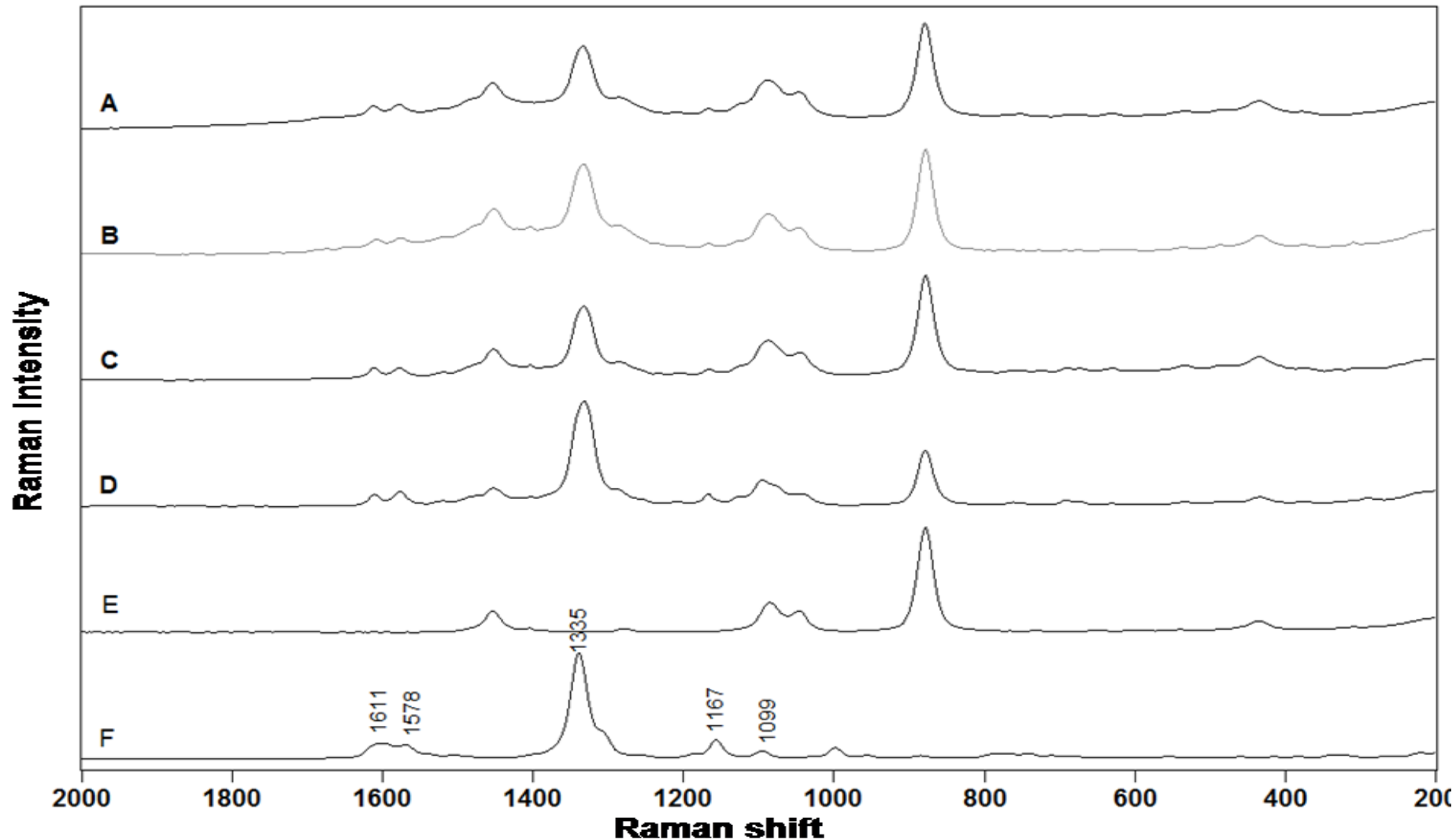
C: Amphetamine.

D: Heroin.

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DFSA; Flunitrazepam in beverages ; Gin





Raman spectra of Flunitrazepam in vodka

(A) 0.01% concentration (w/v %)

(B) 0.02 % concentration (w/v %)

(C) 0.03 % concentration (w/v %)

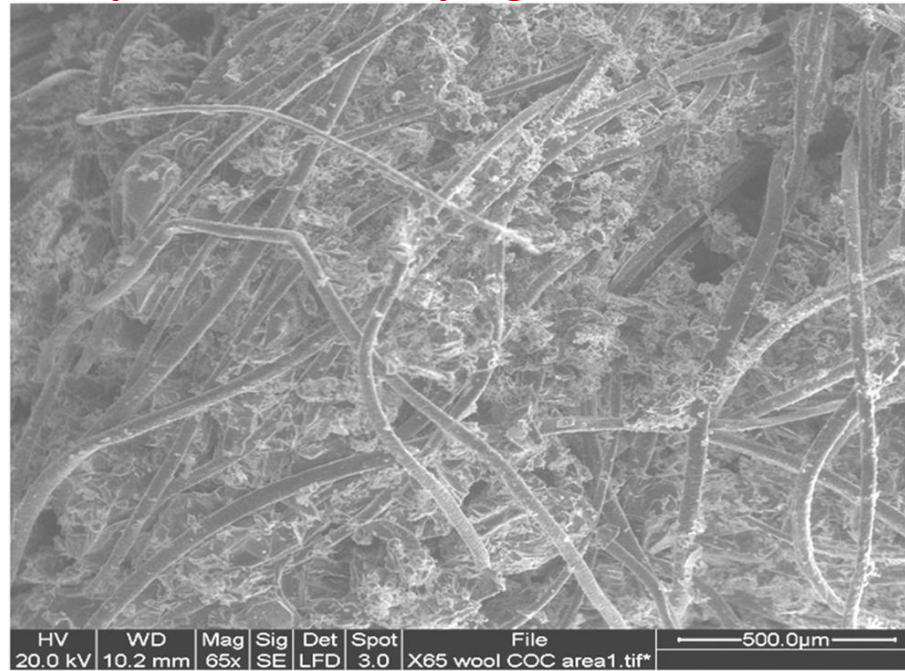
(D) 0.04 % concentration (w/v %)

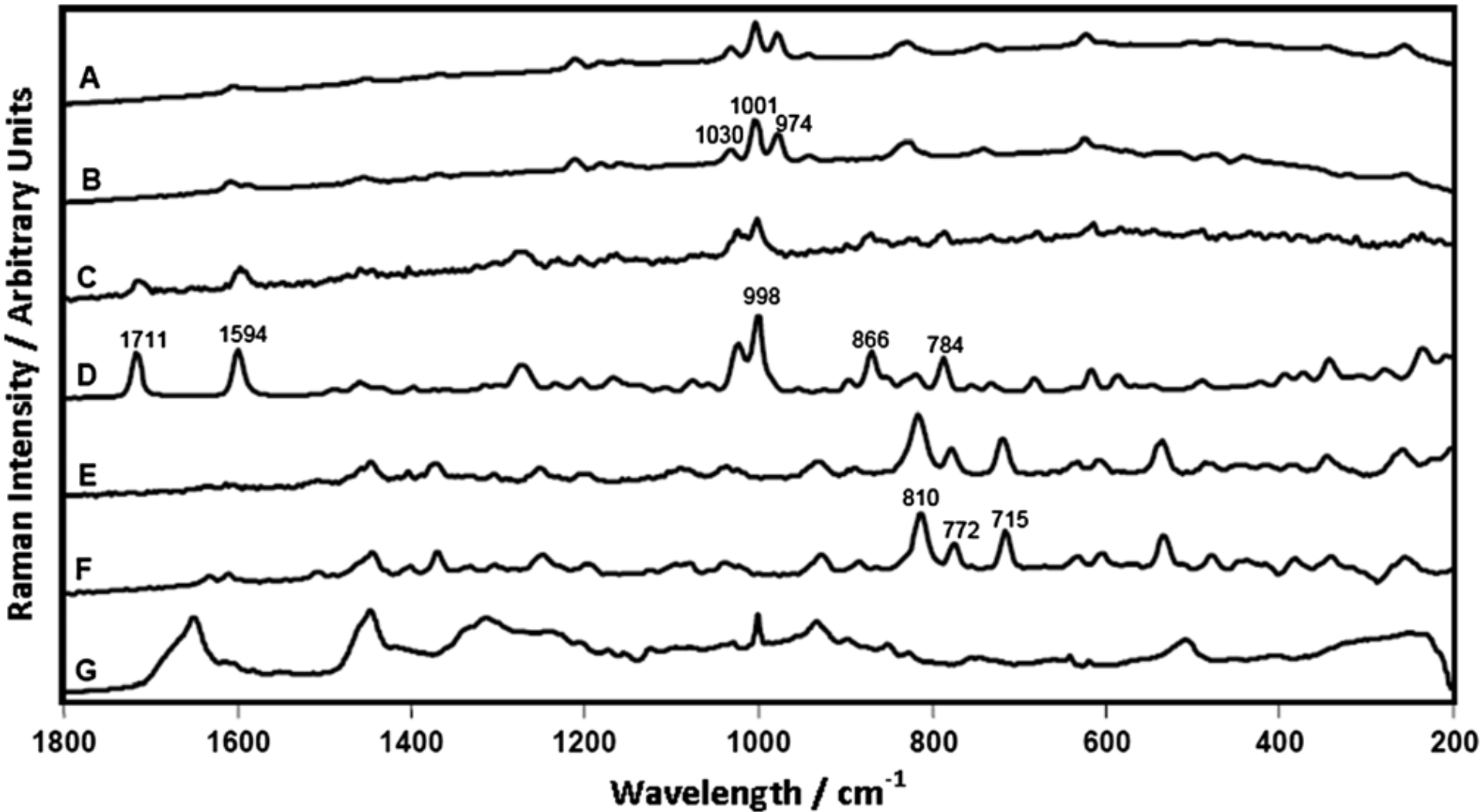
(E) Vodka

(F) Reference flunitrazepam.

Drug smuggling

SEM piece of wool impregnated with cocaine





Raman spectra of drugs of abuse-impregnated wool collected using

(A) Amphetamine (DeltaNu)

(B) amphetamine (RIAS)

(C) cocaine (DeltaNu)

(D) cocaine- (RIAS)

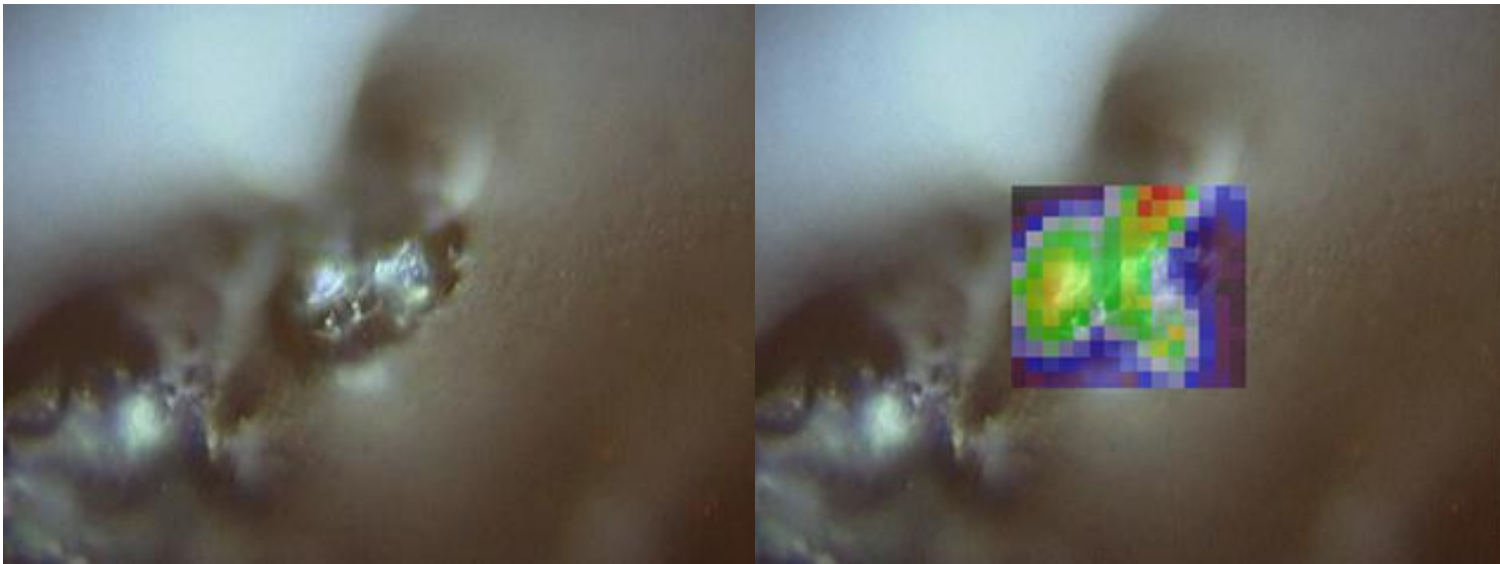
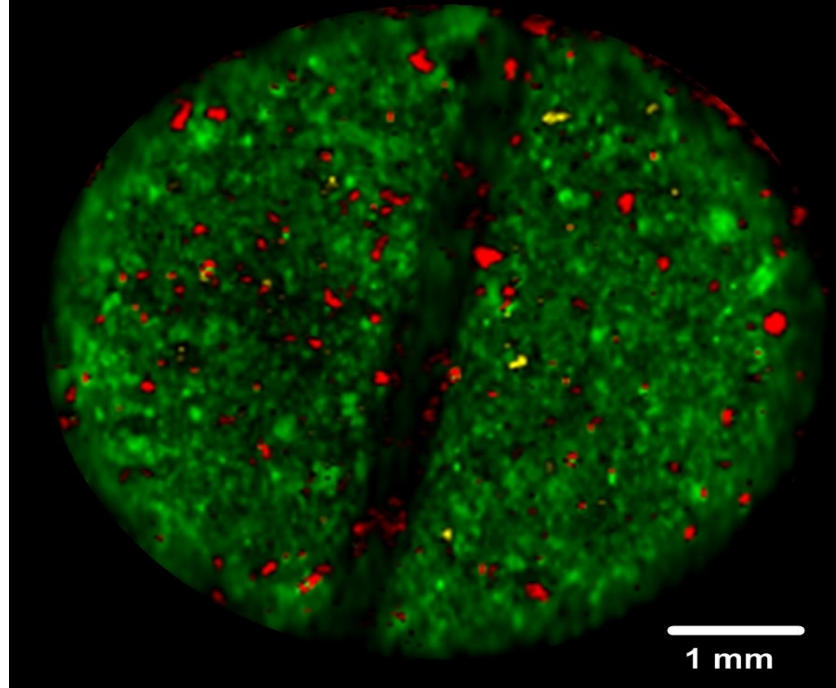
(E) MDMA (DeltaNu)

(F) MDMA(RIAS)

(G) wool .

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MDMA mapping

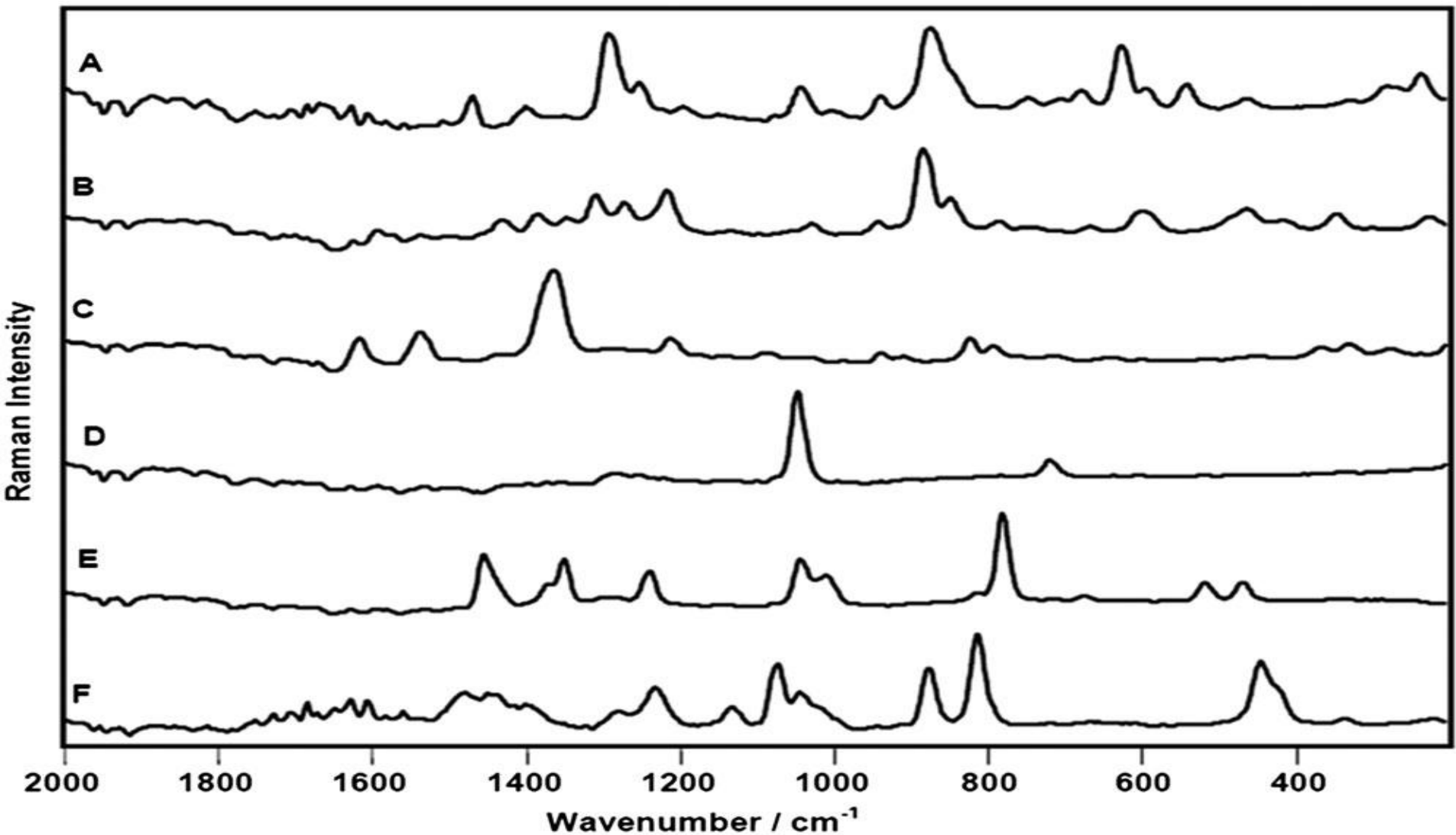


Esam M. A. Ali ,Howell G.M. Edwards , Michael Hargreaves , Ian Scowen , *Anal. Bioanal. Chem.* 2008 ;390(4):1159-66.

II- Explosives

Advantage 1064 is a prototype compact Raman spectrometer
DeltaNu (Laramie, WY, USA). 1064 nm laser





Raman spectra of the explosives and precursors inside plastic bags.

A: RDX

B: PETN.

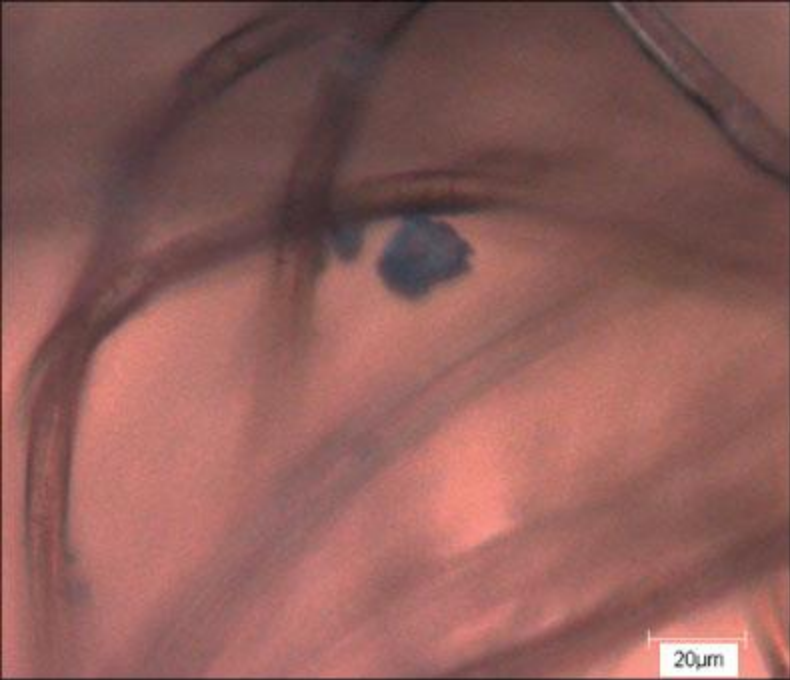
C: TNT

D: Ammonium nitrate.

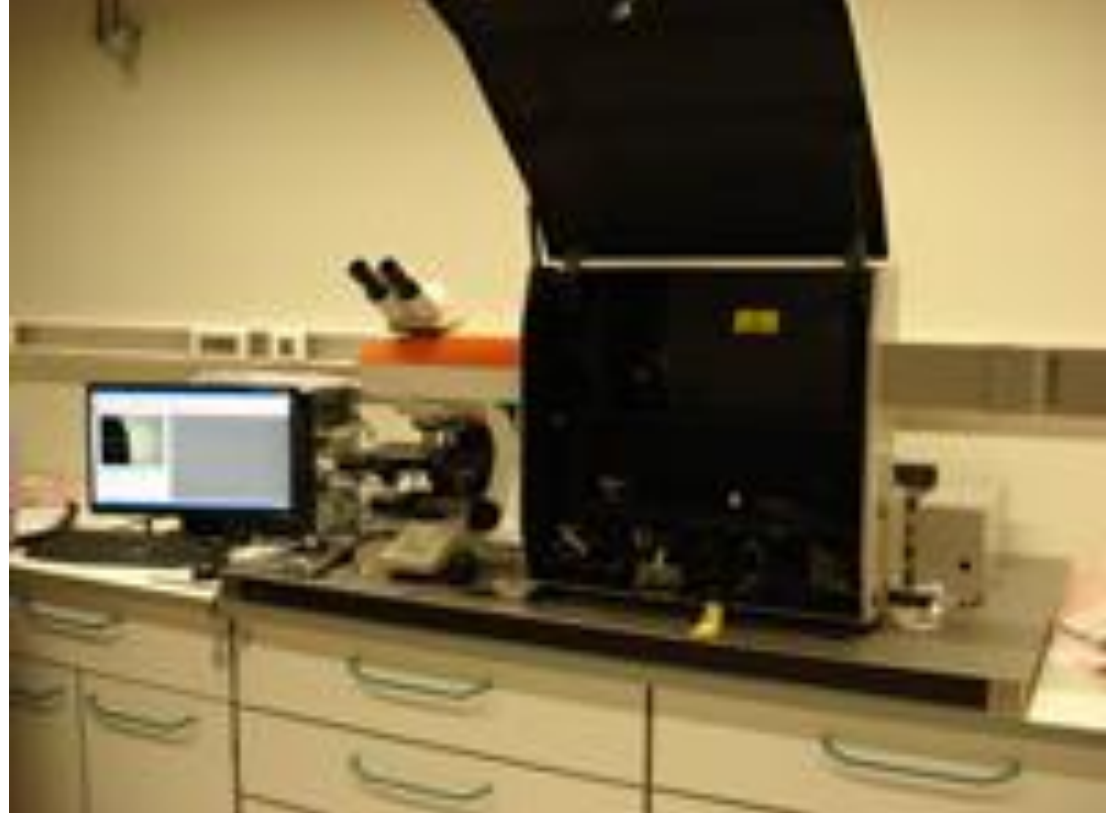
E: Hexamethylenetetramine (HMTA).

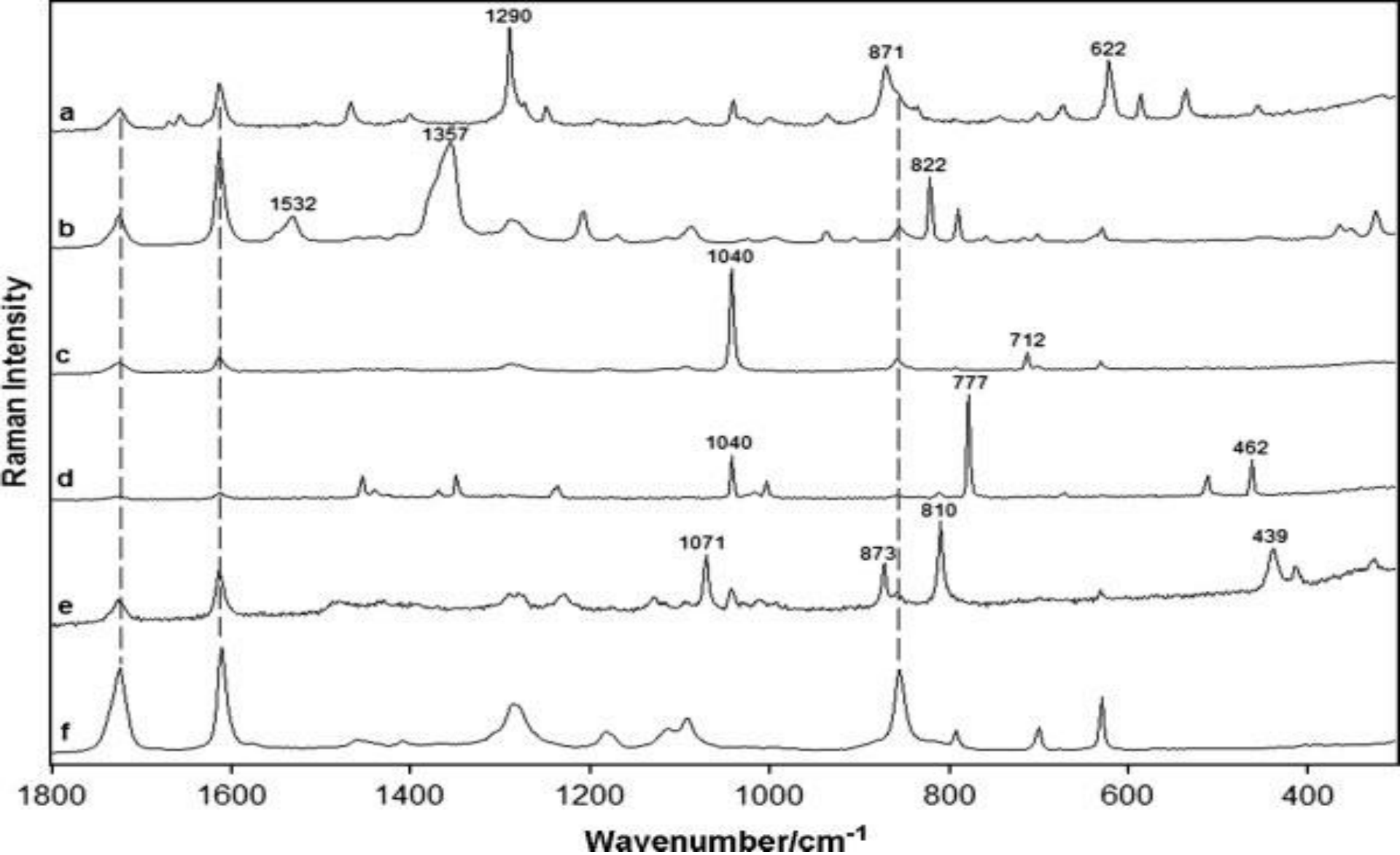
F: Pentaerythritol.

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PETN crystal trapped between polyester fibres.





Raman spectra of

(a) PETN

(c) Ammonium nitrate

(e) Pentaerythritol

(b) TNT

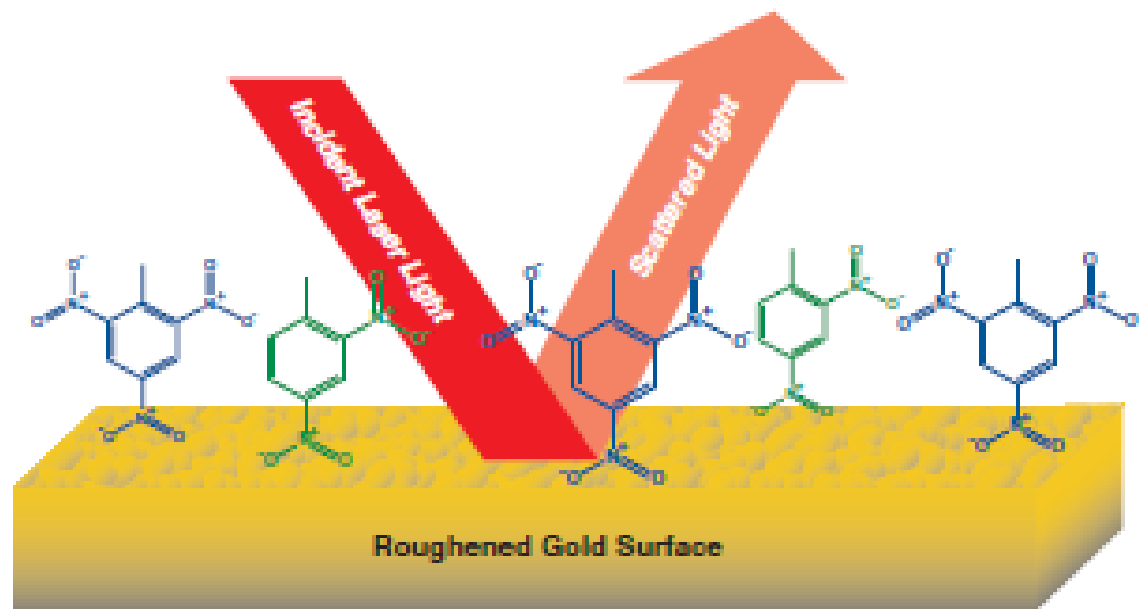
(d) HMTA

(f) Polyester fibres



SERS detection of buried land mines

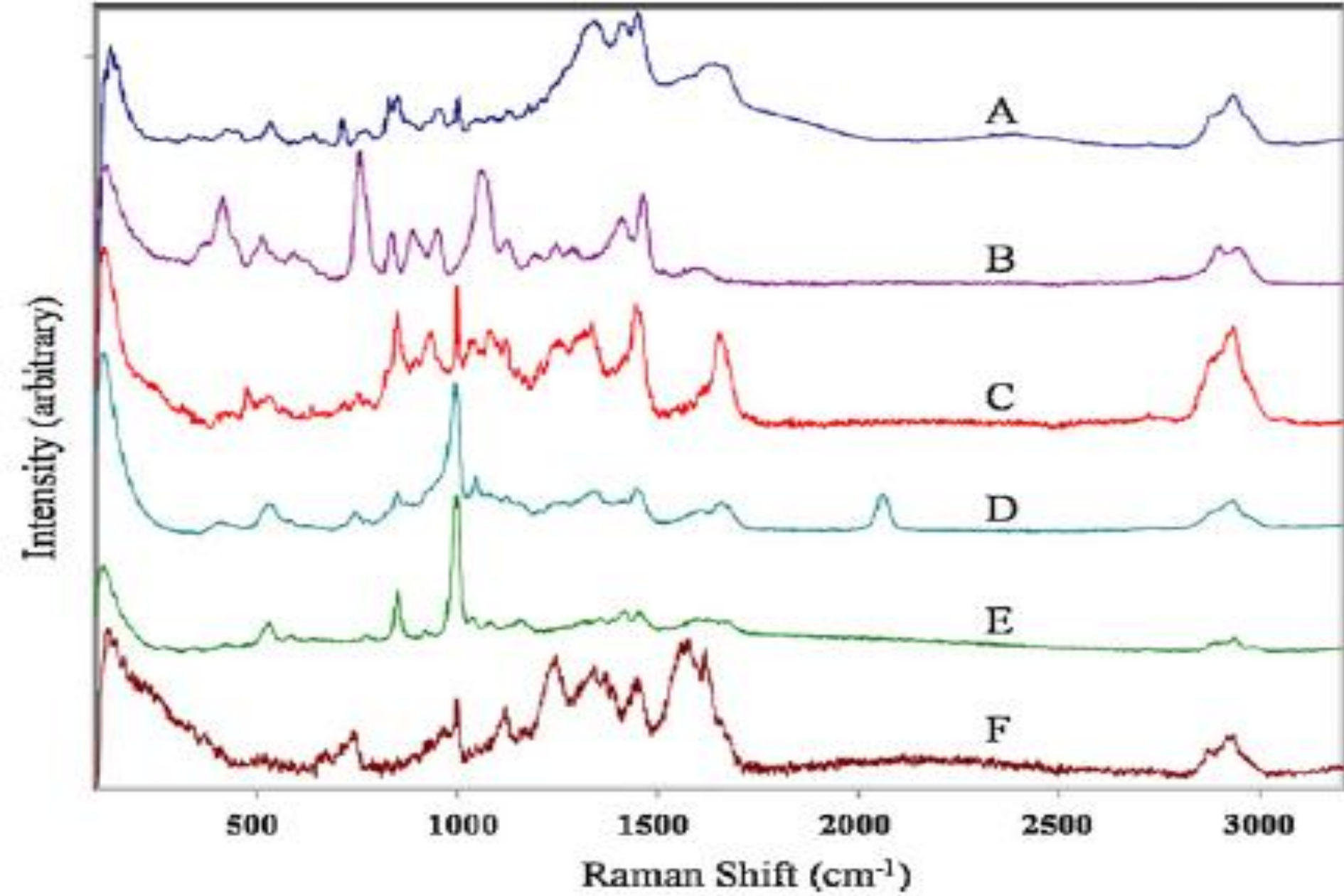
- modern landmines can be constructed without metallic parts and would therefore not be detected with current metal detectors.
- SERS is able to detect the actual explosive material (e.g. TNT, RDX)



SERS measurement of 2,4-DNT and 2,4,6-TNT on a gold substrate.

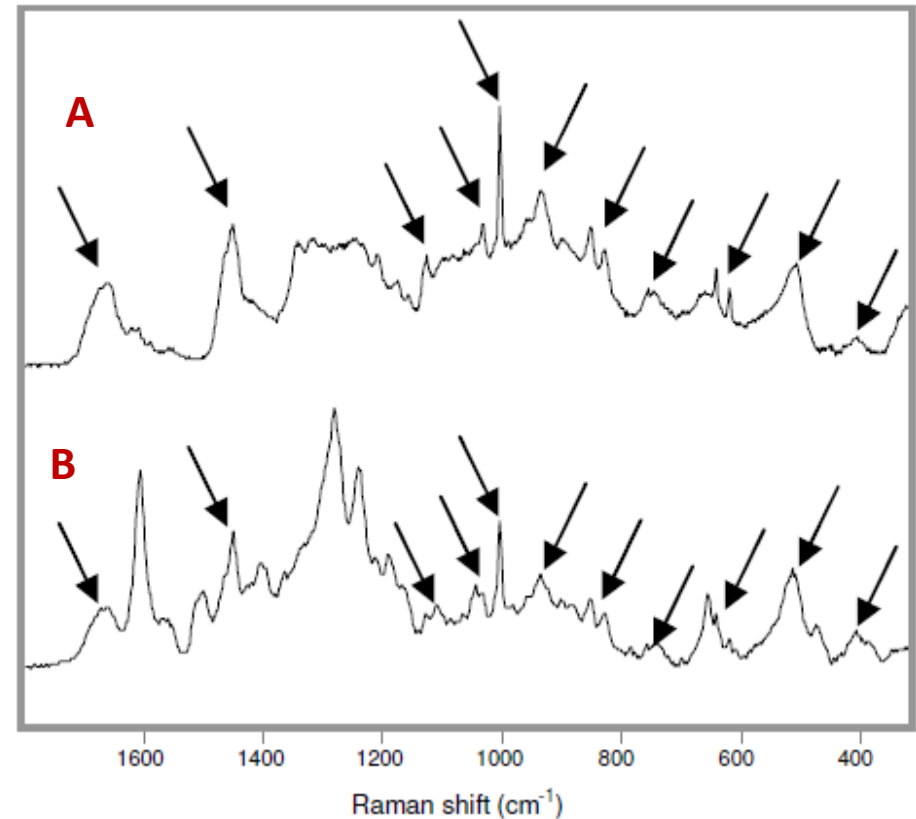
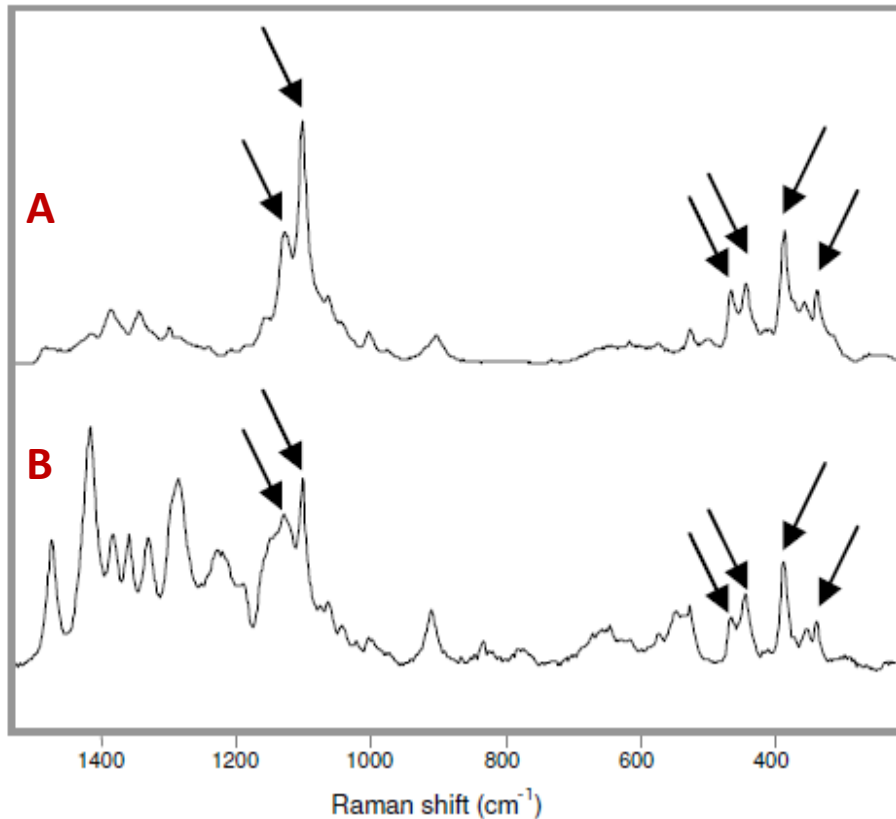
III- Identification of body fluids

- **Destructive presumptive tests**
- **Current simple on-field screening tests do not confirm the presence of a particular fluid**
- **It is crucial that these small quantities are examined as efficiently as possible by non-destructive methods at the crime scene.**
- **Great need of a reliable and ultimately on-field method that can exclusively distinguish between common and uncommon body fluids non-destructively.**
- **The stain or swab could be tested on the field and still be available for further use in the laboratory for DNA analysis**



Raman spectra of human semen (A), canine semen (B), vaginal fluid (C), saliva (D), sweat (E), and blood (F).

IV- Fiber examination



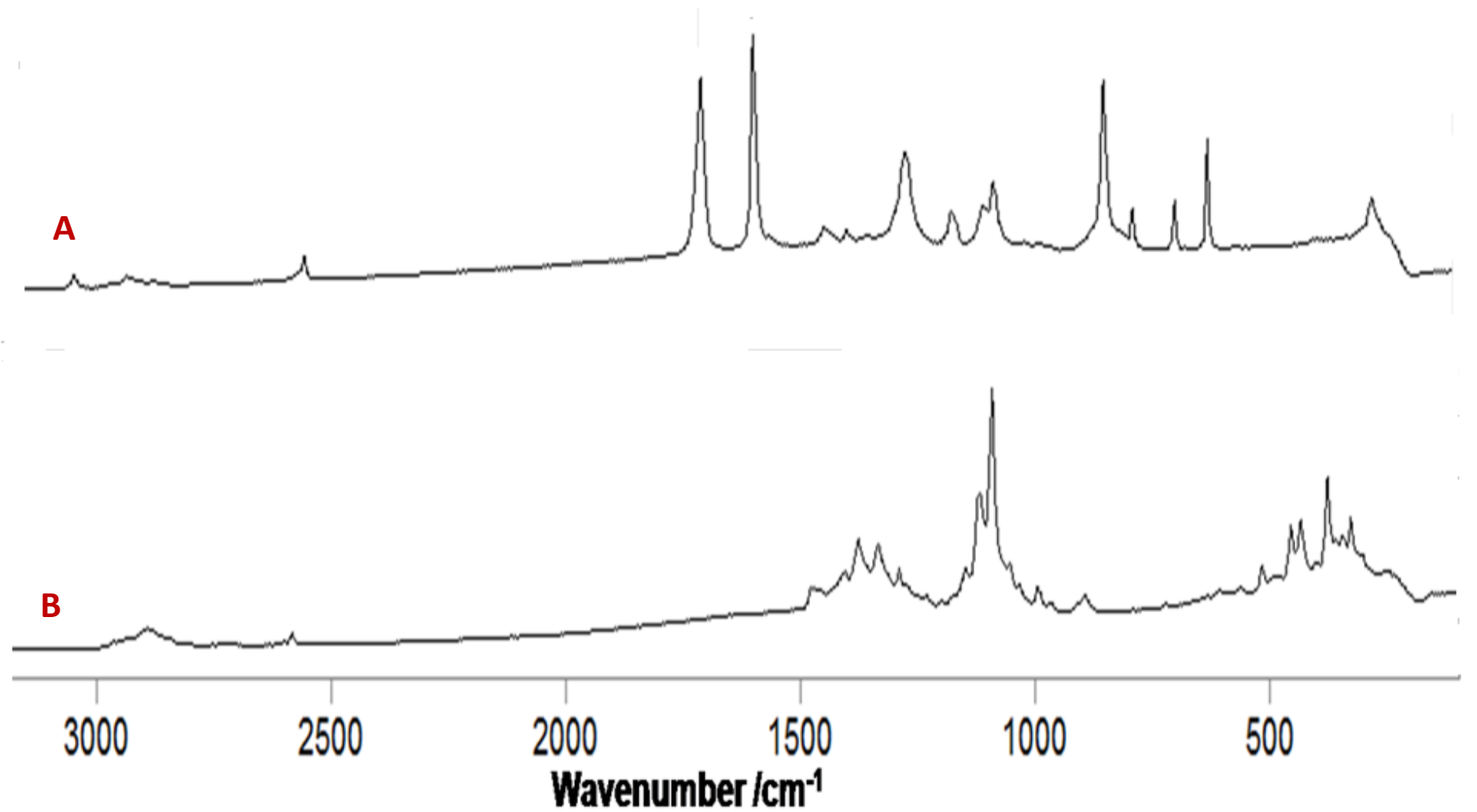
A:undyed cotton fiber

B: red colored cotton fiber

Arrows indicate the bands attributed to the substrate.

A:undyed wool fiber

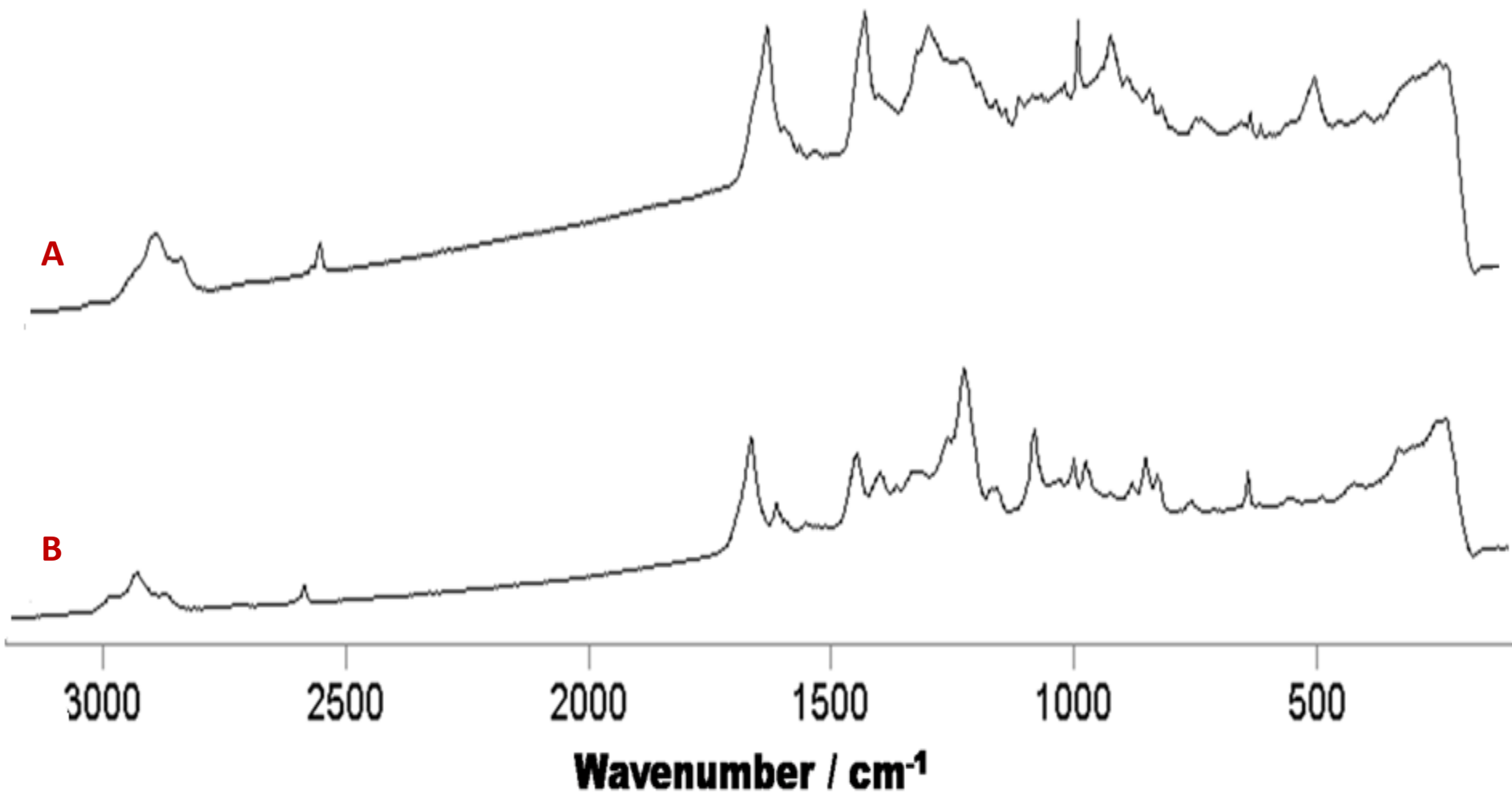
B: red colored wool fiber



spectrum of a single

A: cotton fiber

B: polyester

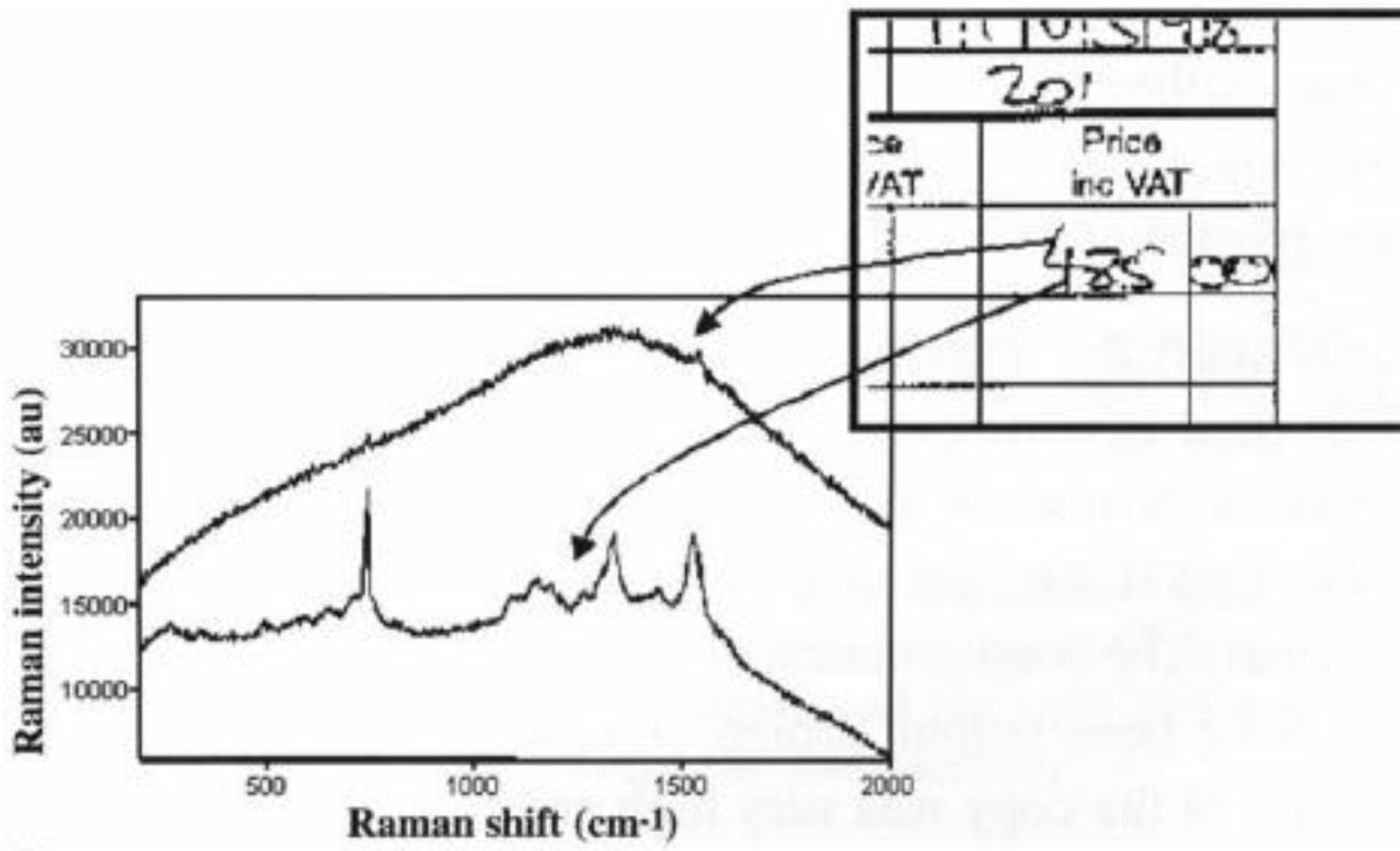


Comparison of Raman spectra of two animal fibers:

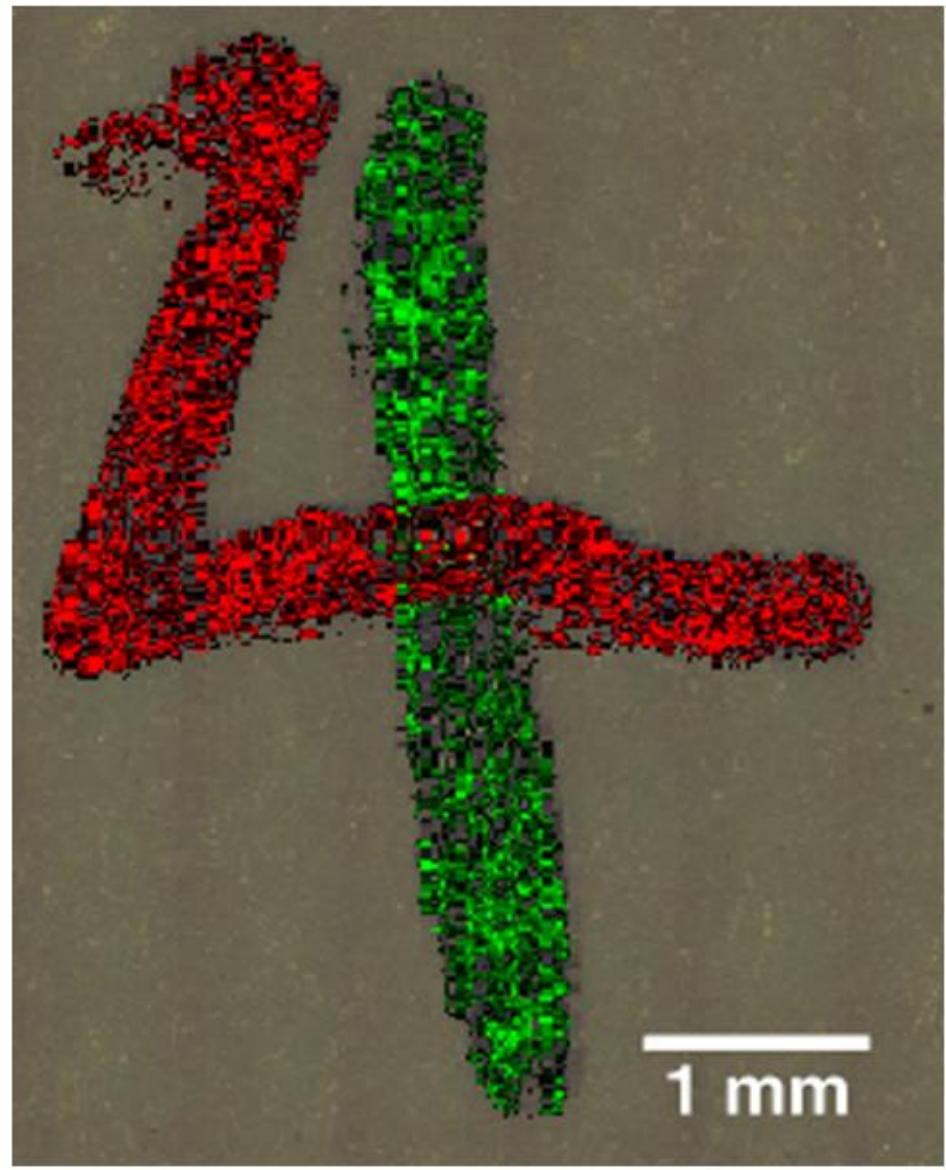
(A) wool

(B) silk

V- inks, questioned documents and fraud

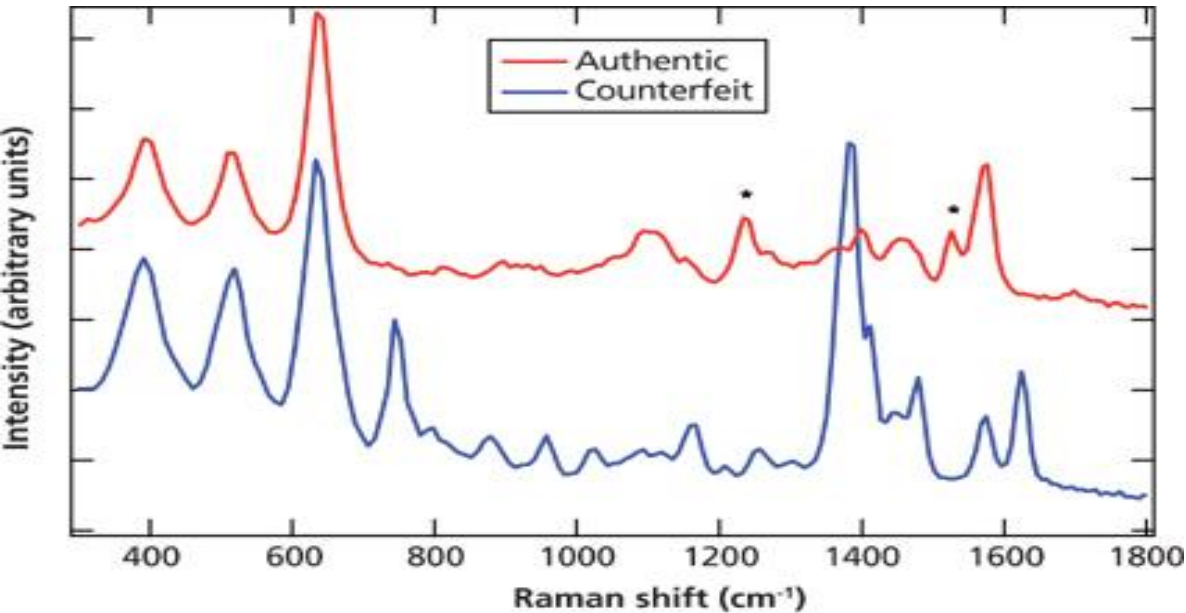


Raman spectra acquired from a suspect '4' on an insurance claim document

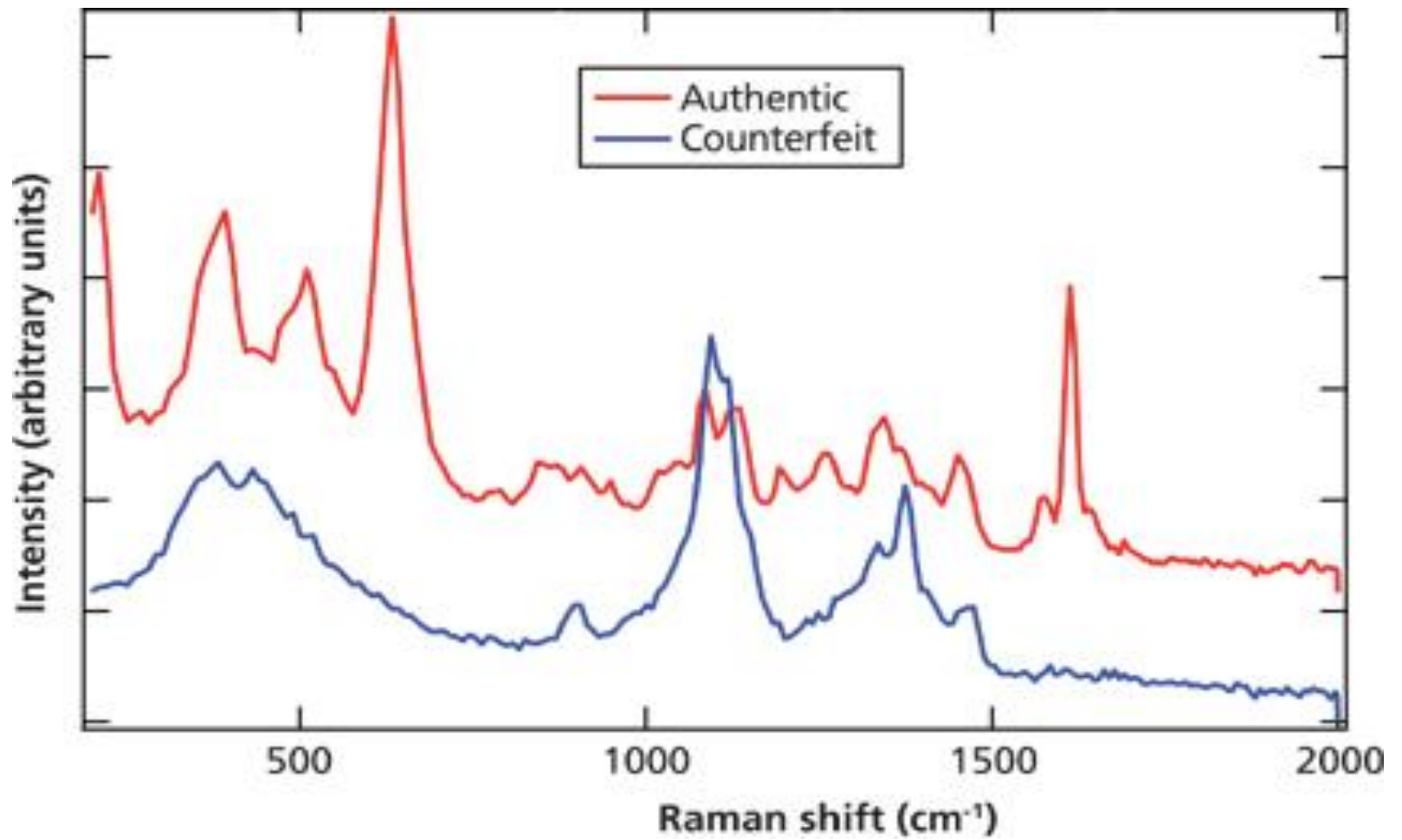


V-COUNTERFEIT PHARMACEUTICALS

Comparing spectral fingerprint of a sample to the known spectral fingerprint of a substance, Raman spectroscopy can identify whether a drug is pure or counterfeit.

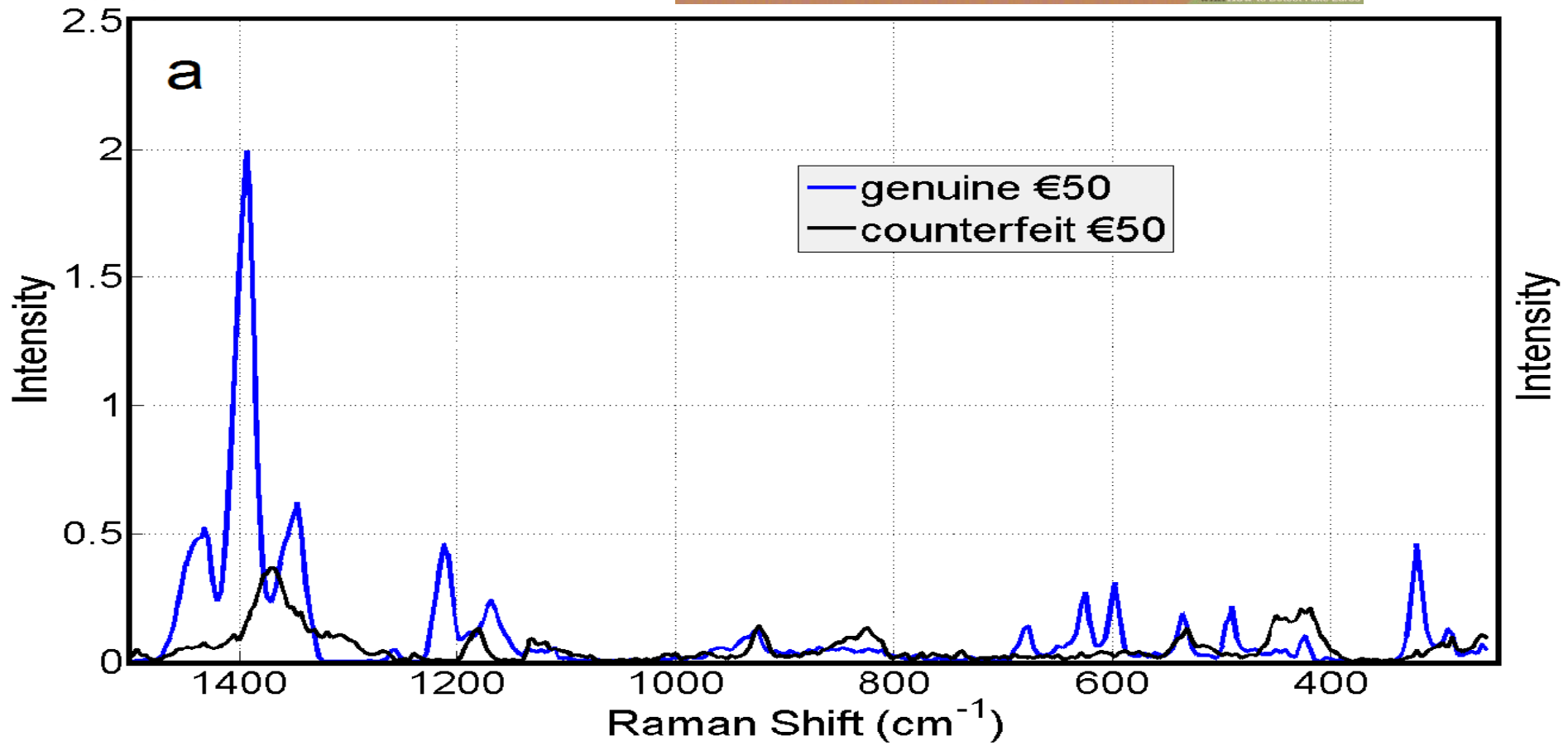


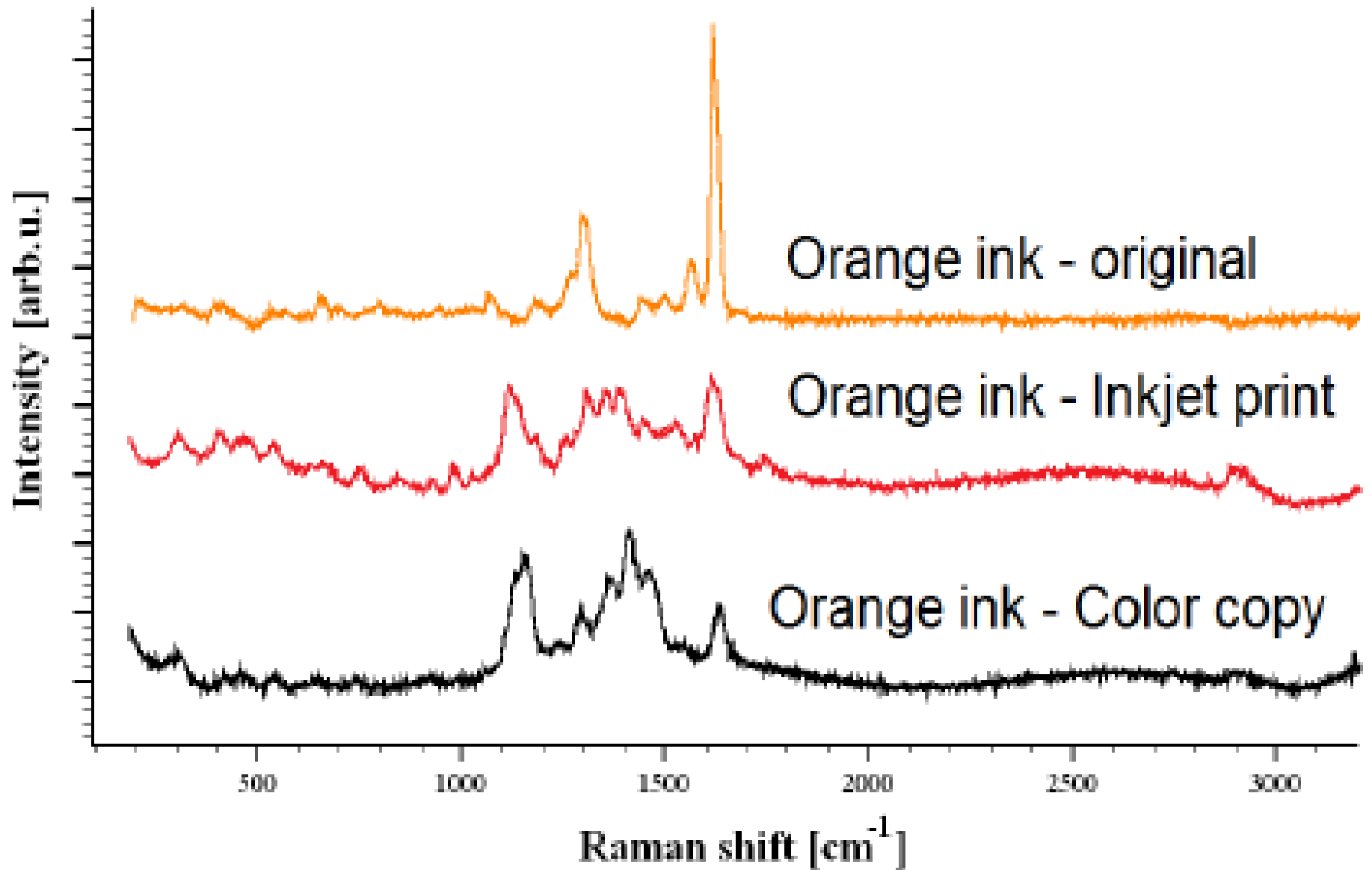
Authentic 50-mg sildenafil citrate (Viagra) tablet and a counterfeit tablet



Authentic and counterfeit hydrogesterone

VI- genuine or forged banknote





Raman spectra of orange ink on genuine 200 CZK note and two imitations

Conclusions

- Raman spectroscopy : chemical composition and structure of materials.
 - Non-contacting and non-destructive : multiple times analysis without damage.
 - Typically no sample preparation is required.
 - Analysis through transparent containers and windows
 - Analysis of samples in water: water is a weak Raman scatter; biological systems.
 - It works on almost all materials: solid, liquids, gases.
- Raman spectroscopy has the potential to be an integral part in the armoury of the forensic analyst as a non-destructive tool for in-situ analysis of a wide range of samples.
- A field-portable Raman spectrometer is a reliable technique that can be used by emergency response teams to rapidly identify unknown samples. The portability and rapidity of the analysis are significant advantages. These criteria are significantly important for law enforcement agencies working in the field and dealing with relatively large numbers of samples on a daily basis.
- Furthermore, the non-destructive and non-contact character of the technique offers a special role for Raman spectroscopy in the first-pass evaluation screening of materials of forensic relevance.