

RAMAN SPECTROSCOPY ITS USE IN FORENSIC DOCUMENT EXAMINATION

Raman Spectroscopy was invented in 1928 by Sir Chandrasekhara Venkata Raman and has been successfully used for many years in the qualitative and quantitative examination of liquids and gases. But only since about 2000 has sufficiently sensitive instrumentation been available to allow dyes and pigments in inks to be examined.

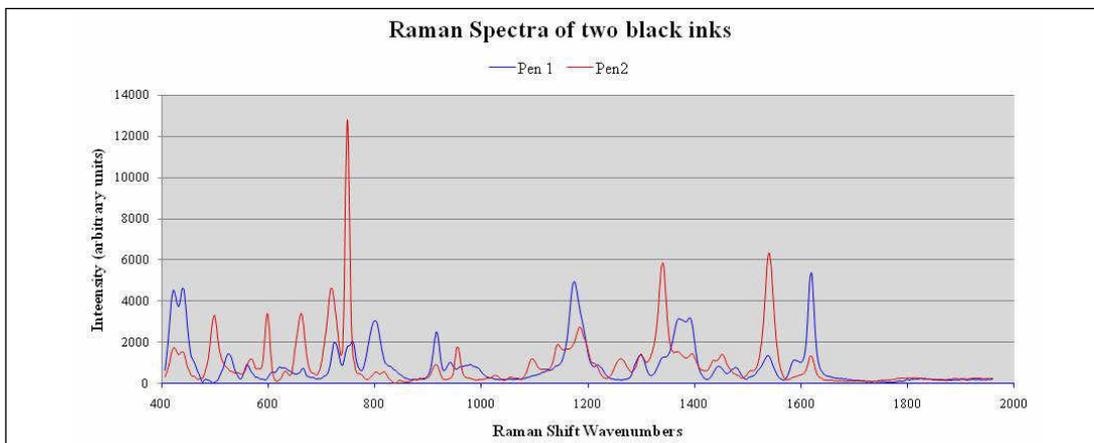
Raman radiation arises when a beam of light is shone onto a sample – some of the light is absorbed by the molecules in the sample and re-emitted at different wavelengths, the pattern of the emitted Raman lines being characteristic of the molecules in the sample. Hitherto it has been necessary to extract dyes and pigments from samples to examine them by Raman Spectroscopy, but new instrumentation employing a pinpoint laser beam and a highly sensitive detector now allows inks to be examined *in situ*, effectively permitting non-destructive testing of materials on paper.

Raman Spectroscopy, though a new technique in the area of Forensic Document Examination, is proving to be a helpful tool to discriminate differences in inks on paper produced by pens and printers. It is also showing promise with photocopy and laser toner deposits on documents.

Foram 685-2 Spectral Comparator

This instrument measures Raman radiation when a tiny beam of laser light is shone onto an area of document under examination. The width of this beam is only 5 μm (five thousandths of a millimetre), and can be focussed onto an ink line, printer or toner deposit with great precision. The laser light is of relatively low energy so no damage is made to the document and a Raman spectrum can be generated quickly.

The illustration below shows the Raman Spectra obtained from two black ballpoint pen inks. The spectra are different, demonstrating that two different pens were used to create the document.



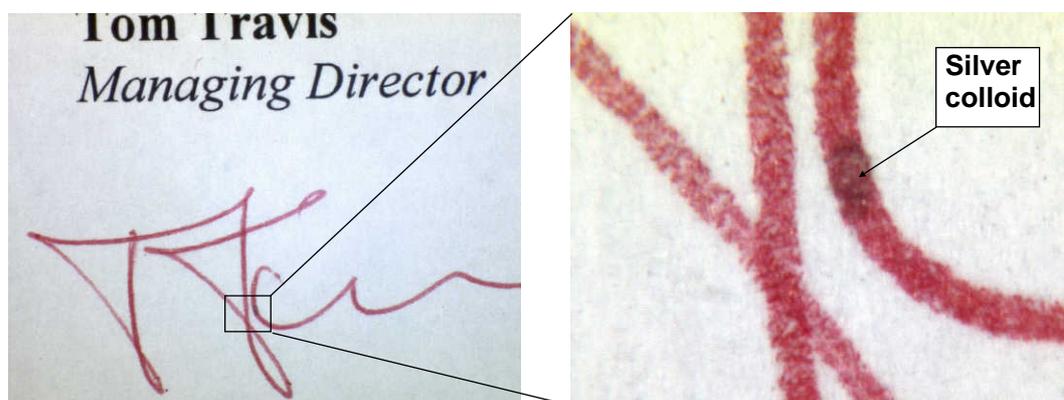
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SERRS Spectroscopy

With some samples, the incident laser light causes the sample to fluoresce. The spectra from such samples have a large fluorescence baseline, making it difficult to see the Raman peaks. Surface Enhanced Resonance Raman Scattering (SERRS) is an enhancement of the technique that improves the Raman spectra by reducing the amount of fluorescence that occurs. It involves painting a thin layer of a silver colloid onto the sample actually *within* the pen line of the sample to be examined. The illustration below shows a magnified image of a pen line where the grey-coloured colloid can just be seen on the surface of the ink line; a red ink has been selected for this demonstration simply because on a more commonly encountered blue or black ink line, the colloid is almost completely invisible!



Though some forensic scientists deem the technique non-destructive, strictly speaking this is not correct - there will be some microscopic alteration to the document, but its evidential value will remain unaltered. The Giles Document Laboratory always seeks written approval from Clients to carry out SERRS Spectroscopy on a document.

Raman Spectroscopy remains relatively new in the field of Forensic Document Examination and The Giles Document Laboratory is one of the very few laboratories pioneering this field with this technique. After more conventional non-destructive techniques have been exhausted, Raman Spectroscopy offers a further avenue for the discrimination of inks.

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