

SURFACE ENHANCED RESONANCE RAMAN SCATTERING (SERRS) SPECTROSCOPY – STUDY ON INKS

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ABSTRACT: Surface Enhanced Resonance Raman Scattering (SERRS) spectroscopy can overcome many of the limitations of conventional Raman spectroscopy in ink analysis, specifically dominant fluorescence and weak Raman signals.

In this study we show how, with the SERRS technique, we could obtain detailed spectra from ink samples that were weak Raman scatterers or exhibited dominant levels of fluorescence when analysed previously. Further to this, it was possible to differentiate samples based on their SERRS spectra that could not be otherwise discriminated with conventional infrared techniques (e.g. VSC).

KEY WORDS: Raman spectroscopy; SERRS; Ink; Toner; Questioned documents.

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INTRODUCTION

The use of Raman spectroscopy in forensic examinations is increasing. However there are certain samples that are not readily suited to conventional Raman spectroscopy. These mostly include fluorescent materials or samples with intrinsically weak scattering cross-sections. Examples of this type commonly seen in forensic document examination are pen inks that are fluorescent in the near infrared and toner samples that show only weak Raman signals.

A recent article by White et al. [3], has demonstrated that these limitations can largely be overcome using the technique of SERRS. Raman signals are enhanced through resonance effects [1] and by SERRS [2]. The resonance enhancement would be expected through most of the visible spectrum, as the dye components of inks tend to have broad absorption bands in this spectral region, however the increase in Raman signal will be accompanied by a corresponding increase in the fluorescence yield. The surface enhancement is achieved through use of a colloidal silver aggregate. Not only are the Raman signals further enhanced, but the presence of colloidal silver largely quenches the fluorescence.

For SERRS to be effective, relevant sample molecules must either be bound to or held in close proximity to the silver colloid. This is achieved here through the use of an aggregating agent, poly-L-lysine.

METHODS AND MATERIALS

All measurements were made using a Foram 685 Raman Spectral Comparator (Foster and Freeman Ltd., UK). The laser wavelength was 685 nm. The measurements were taken on the lowest power setting (~0.5 mW). A colloidal silver solution and poly-L-lysine aggregating agent were used for the SERRS measurements.

The aggregating agent was applied to a small portion of the ink sample using a mapping pen and then allowed to dry (approximately one minute). The colloidal silver was then applied to the same portion of ink using a different mapping pen and allowed to dry. Typically an area of 1 mm² or less was treated in this way.



Fig. 1. The image of pen stroke after the silver colloid treatment.

The SERRS technique is considered non-destructive as no sample is removed from the document, and there is only a microscopic effect to the sample surface.

Figure 1 shows the image of pen stroke after the silver colloid treatment. The two vertical lines are pencil marks between which the sample has been treated. The pen stroke outside the two pencil marks has not been treated.

Data acquisition times were typically less than 1 second, with spectra averaged over several readings.

Inks analysed for this study were as follows:

- blue ball point pen inks,
- black ball point pen inks,
- blue fluid inks,
- black fluid inks,
- red fluid inks,
- green fluid inks,
- inkjet printer inks.

RESULTS

Figure 2 shows examples of the conventional Raman spectrum from a fluorescent ink sample.

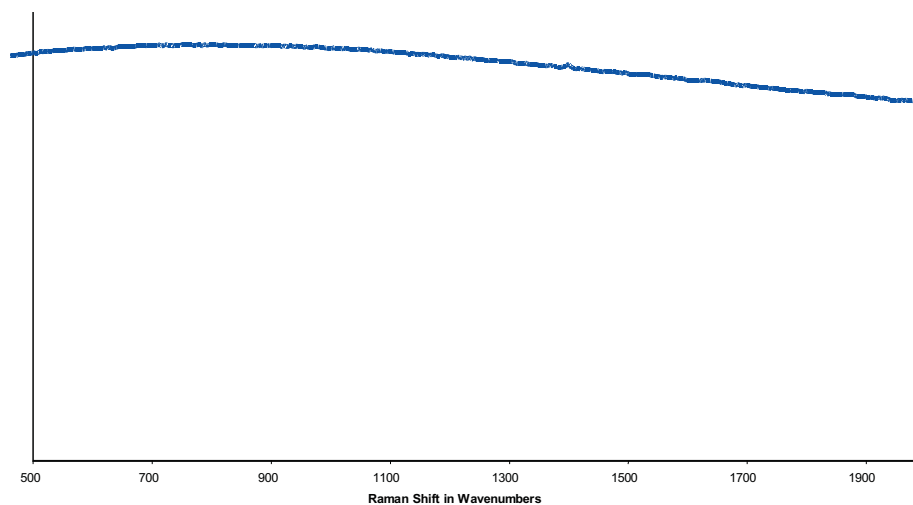


Fig. 2. Examples of the conventional Raman spectrum from a fluorescent ink sample.

The fluorescence emitted is many, many times more intense than any Raman signal, saturating the sensitive Raman detector and masking the Raman signal.

Figure 3 shows an example of a typical SERRS spectrum from an ink sample.

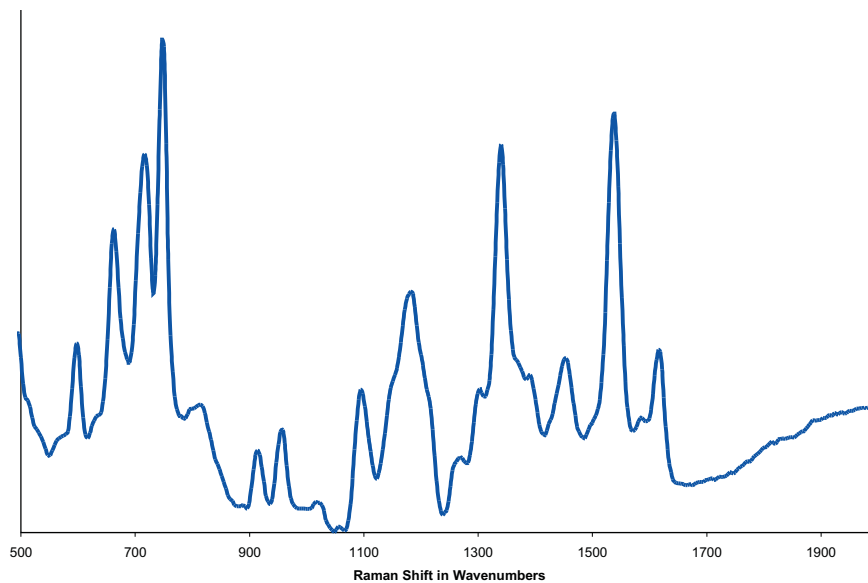


Fig. 3. An example of a typical SERRS spectrum from an ink sample.

The application of the SERRS techniques quenches the fluorescence and enhances the Raman signal of the dye components of the ink. Fluorescent inks with different dye components may give similar results when viewed under the VSC, or with normal Raman spectroscopy. However, when SERRS is used, these inks may be discriminated as they display peaks at different wavenumbers in their SERRS spectra.

DISCRIMINATION OF SAMPLES

The Raman and SERRS spectra of each ink were compared to every other ink of the same colour and type. The discriminating power for Raman, SERRS and Raman and SERRS combined was then calculated for each sample group. These are detailed in Table I.

TABLE I. THE DISCRIMINATING POWER FOR RAMAN, SERRS AND RAMAN AND SERRS

Sample	Method	Pairs discriminated	Discriminating power
Blue ball point – 325 pairs	Raman	153	47.1%
	SERRS	193	59.4%
	Combined	262	80.6%
Black ball point – 325 pairs	Raman	188	57.8%
	SERRS	109	33.5%
	Combined	213	65.5%
Blue fluid ink – 1953 pairs	Raman	925	47.4%
	SERRS	1644	84.2%
	Combined	1700	87.0%
Black fluid ink – 1770 pairs	Raman	1315	74.3%
	SERRS	1635	92.4%
	Combined	1700	96.0%
Green fluid ink – 630 pairs	Raman	218	34.6%
	SERRS	458	72.7%
	Combined	460	73.0%
Red fluid ink – 1128 pairs	Raman	318	28.2%
	SERRS	1046	92.7%
	Combined	1071	94.9%

CONCLUSIONS

It has been shown that SERRS spectroscopy dramatically enhances the usefulness of Raman based techniques. Samples which are either inherently IR fluorescent or weak Raman scatterers may now yield quality spectra which can be used for discrimination. It is likely that SERRS spectroscopy will have wider applications in many aspects of Forensic Science, especially in questioned document examination.

References:

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