RAMAN SPECTROSCOPY OF INK ON PAPER

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ABSTRACT: Blue and black ballpoint pen as well as blue, black, green and red fluid inks on paper are examined by Raman spectroscopy. The quality of the Raman spectra is strongly dependent on the excitation wavelength. Therefore, two different spectrometers with different excitation wavelengths have been tested. In addition, Surface Enhanced Resonance Raman Spectroscopy (SERRS) was used. Application of SERRS helps to avoid fluorescence and enhance certain Raman signals. Because of the minute amount of reagent applied to the ink-line, this procedure may still be regarded as non-destructive. The resulting Raman spectra are compared and classified. Classification results are compared with a classification of the inks by thin layer chromatography. An evaluation of the results will show to what extent Raman spectroscopy may be useful in questioned document examination.

KEY WORDS: Raman spectroscopy; Ink; Document examination.

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INTRODUCTION

Recently we see an increasing number of applications in Raman spectroscopy. Thermoelectrically cooled CCD array detectors and techniques like surface enhanced resonance Raman spectroscopy (SERRS) enable an increase in sensitivity sufficient for applications in forensics [1]. In Raman spectroscopy the analyte is excited with monochromatic laser-light. The scattered light (rayleigh scattering) contains the excitation wavelength, which can be removed by holographic filters, and signals at longer (Stokes shift) and shorter wavelength (anti stokes shift). Usually the Stokes signals are more intensive and therefore monitored as the Raman spectrum.

Position and intensity of Raman signals depend on the maximum absorption wavelength of the analyte. Therefore appropriate excitation wavelengths are needed. Fluorescence of the analyte or the substrate may cover the Raman signals, which can be avoided by blocking the fluorescence.

In document examination we are mainly interested in inks and dyes therein. We are confronted with a great variety of dyes of different hues, which means they have different absorption maxima. The dyes belong to different chemical classes such as inorganic and organic pigments, acid and ba-

sic dyes, substantive and reactive dyes, triphenylmethane dyes, azo dyes etc.

EXPERIMENTAL

For this study we used two Raman spectrometers: A FORAM 685 from Foster & Freeman Ltd. and a LabRam Infinity from Dilor GmbH. The FORAM 685 offers one excitation wavelength at 685 nm. The spectral range is between 400 and 2000 cm^{-1} with a resolution of 8 cm^{-1} . The laser power on the samples was about 1.5 mW. The LabRam Infinity offers several laser sources, from which we used 514, 633 and 785 nm. The spectral range we used is between 60 and 3000 cm^{-1} with a resolution of 4 cm^{-1}. The laser power on the samples can be tuned from 0 to 6 mW.

We examined ink lines drawn on white office paper of 26 blue and 26 black ball point pen inks and 63 blue, 60 black, 36 green and 48 red fluid inks. The inks were examined directly without any sample preparation and after subsequently treating the samples with a solution of poly-L-lysine and a silver colloid to obtain SERRS spectra (SERRS 1). In some cases additional application of an ascorbic acid solution (SERRS 2) leads to better results.

RESULTS AND DISCUSSION

The discrimination power obtained by the FORAM 685 is shown in Table I. In most cases the application of the SERRS reagents leads to a distinct increase in the discrimination power. The decrease in case of the black ball point pen inks is due to the fact, that in the native spectra the shape of the fluorescence can be used as a criterion for differentiation. The SERRS spectra show no fluorescence.

TABLE I. DIFFERENTIATION OF INKS BY FORAM 685

Ink	Raman	SERRS1	SERRS2
Blue ball point	47.1%	80.3%	–
Black ball point	57.8%	33.5%	–
Blue fluid ink	47.4%	82.7%	84.2%
Black fluid ink	74.3%	92.4%	83.2%
Green fluid ink	34.6%	67.1%	72.7%
Red fluid ink	28.2%	87.9%	92.7%

Among optical examination TLC is commonly used for differentiation of inks. Figure 1 shows the TLC results of 19 blue ball point inks some of which we are able to distinguish and some which show identical chromatograms. We take an exemplary look at the first four inks. We cannot distinguish between inks 1 and 2 or inks 3 and 4, but we can easily see the differences between the two pairs.

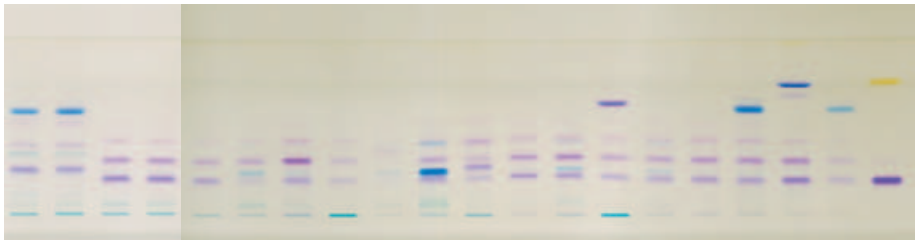

Fig. 1. TLC results of 19 blue ball point inks.

The Raman spectra obtained with the FORAM 685 and SERRS 1 lead to the same conclusion: No differentiation between inks 1 and 2 or inks 3 and 4 respectively, but we see distinct differences between the two pairs (Figures 2–4).

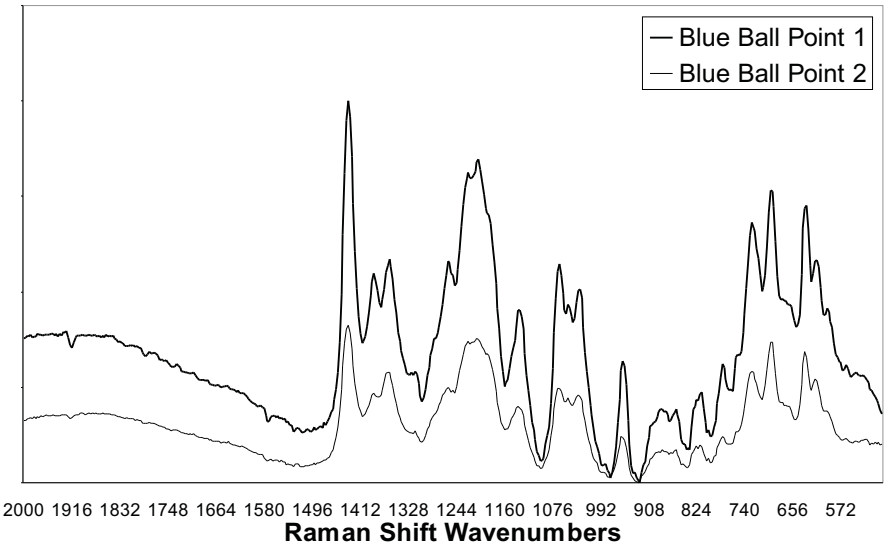

Fig. 2. Raman spectra of blue ball point inks 1 (blue) and 2 (magenta), FORAM 685, SERRS 1.

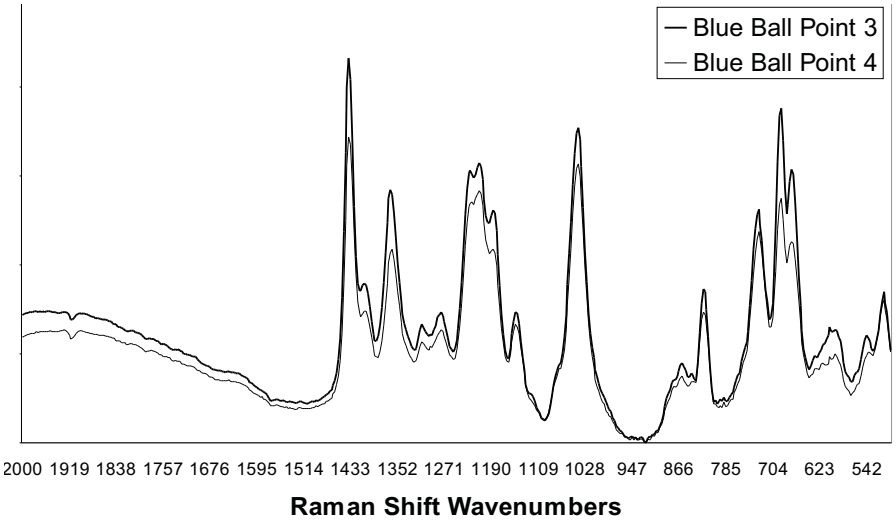

Fig. 3. Raman spectra of blue ball point inks 3 (blue) and 4 (magenta), FORAM 685, SERRS 1.

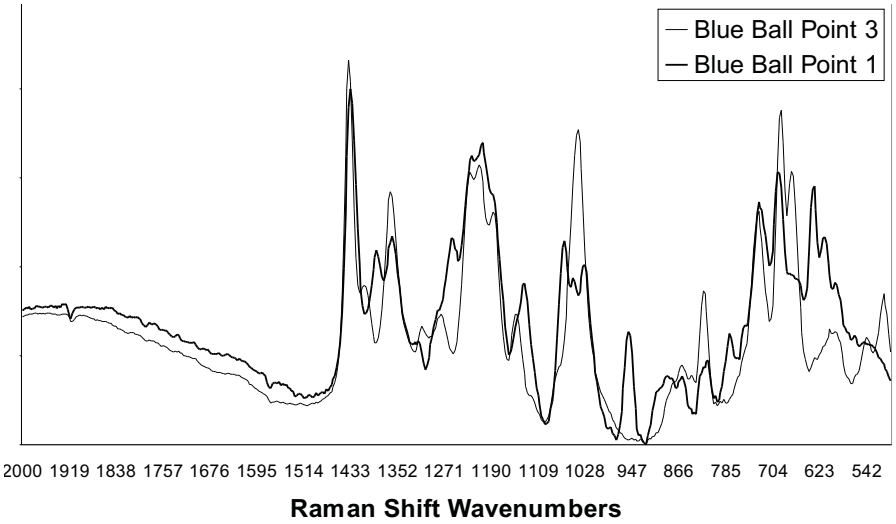

Fig. 4. Raman spectra of blue ball point inks 3 (blue) and 1 (magenta), FORAM 685, SERRS 1.

Figure 4 shows differences in the region of lower wavelengths between the Raman spectra of blue points 1 and 2 obtained with the LabRam Infinity (ex-λ 633 nm, SERRS 1). But it has not been ball checked yet, if these differences are due to different spectroscopic properties of the inks or caused by an artefact. Figure 6 shows no difference between ball point 3 and 4. Whereas Figure 7 shows a distinct difference between ball points 1 and 3.

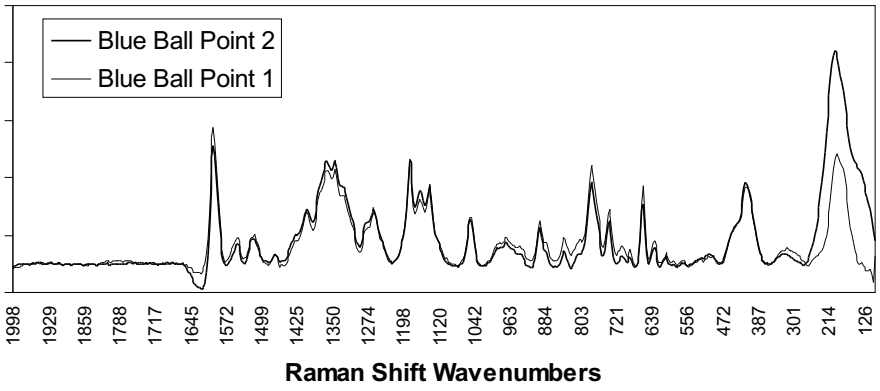

Fig. 5. Raman spectra of blue ball point inks 1 (blue) and 2 (magenta), LabRam Infinity, ex-λ 633 nm, SERRS 1.

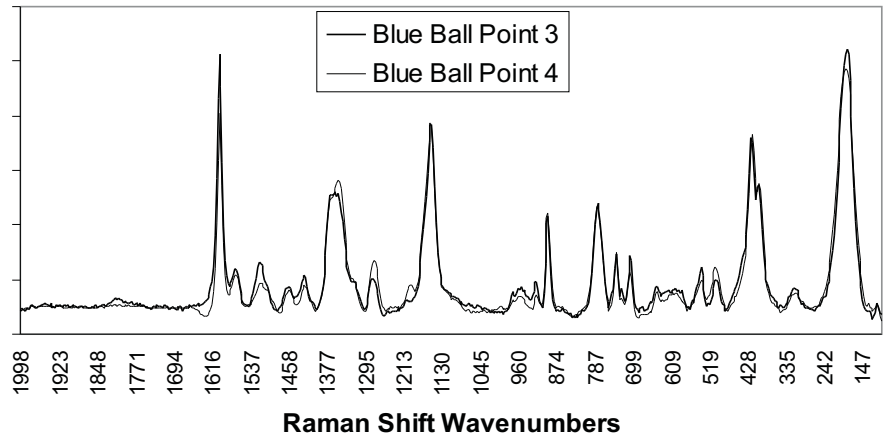

Fig. 6. Raman spectra of blue ball point inks 3 (magenta), and 4 (blue), LabRam Infinity, ex-λ 633 nm, SERRS 1.

Figures 8 and 9 show superimposed spectra obtained with both different spectrometers of ball point 1 and 3 respectively. The quality of the spectra looks comparable. The LabRam Infinity offers greater spectral range and higher resolution, which may contain additional information.

An advantage of Raman spectroscopy compared with TLC is its non-destructive application to documents. Furthermore, for TLC we need to extract the ink from the paper, which is not always possible. Figures 10 and 11 show SERRS 1 spectra of blue gel pen inks, which are easily to distinguish.

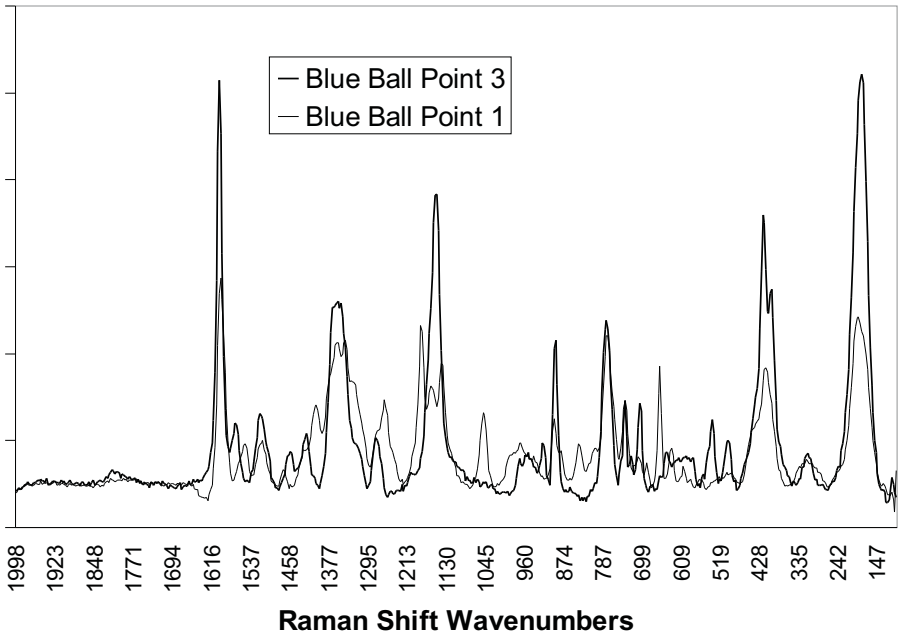

Fig. 7. Raman spectra of blue ball point inks 1 (blue) and 3 (magenta), LabRam Infinity, ex-λ 633 nm, SERRS 1.

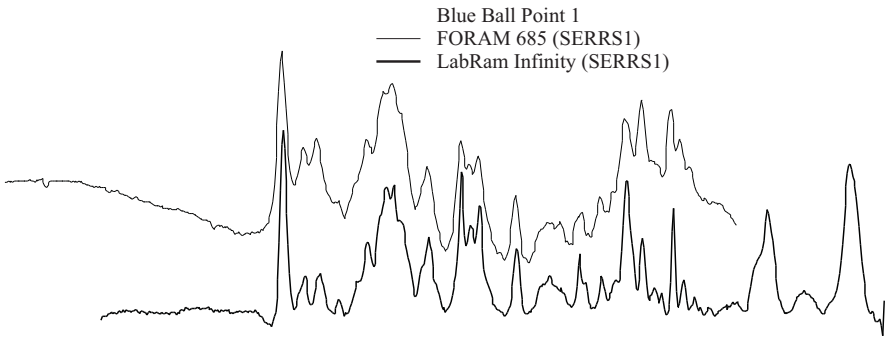

Fig. 8. Raman spectra of blue ball point ink 1, FORAM 685 (magenta) and LabRam Infinity (blue), SERRS 1.

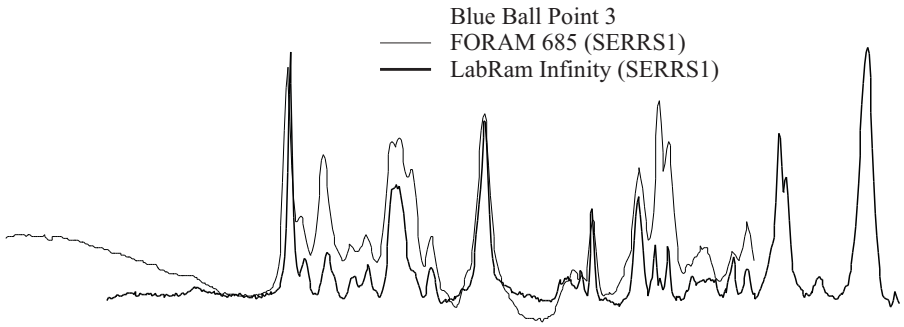

Fig. 9. Raman spectra of blue ball point inks 3, FORAM 685 (magenta) and LabRam Infinity (blue), SERRS 1.

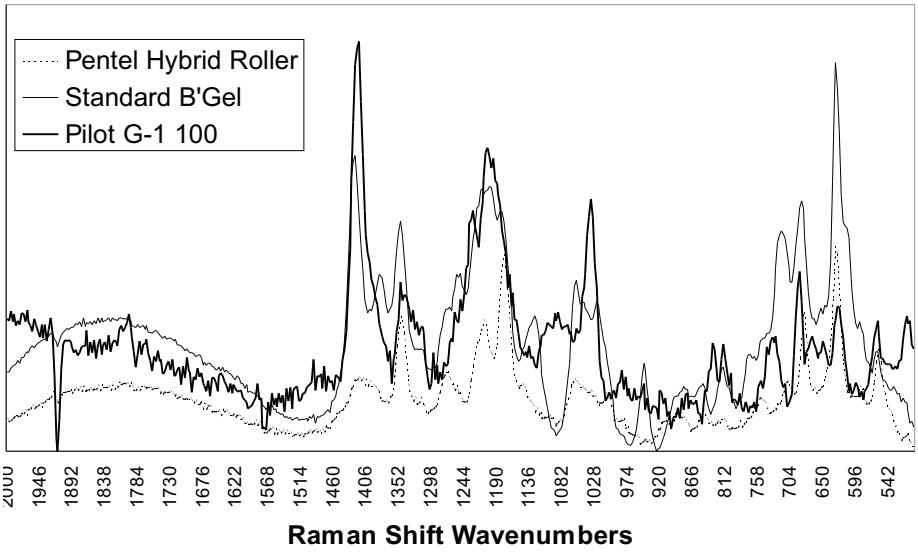

Fig. 10. Raman spectra of blue gel pen inks, Pentel Hybrid Roller (magenta), Standard B'Gel (red), Pilot G-1 100 (blue), FORAM 685, SERRS 1.

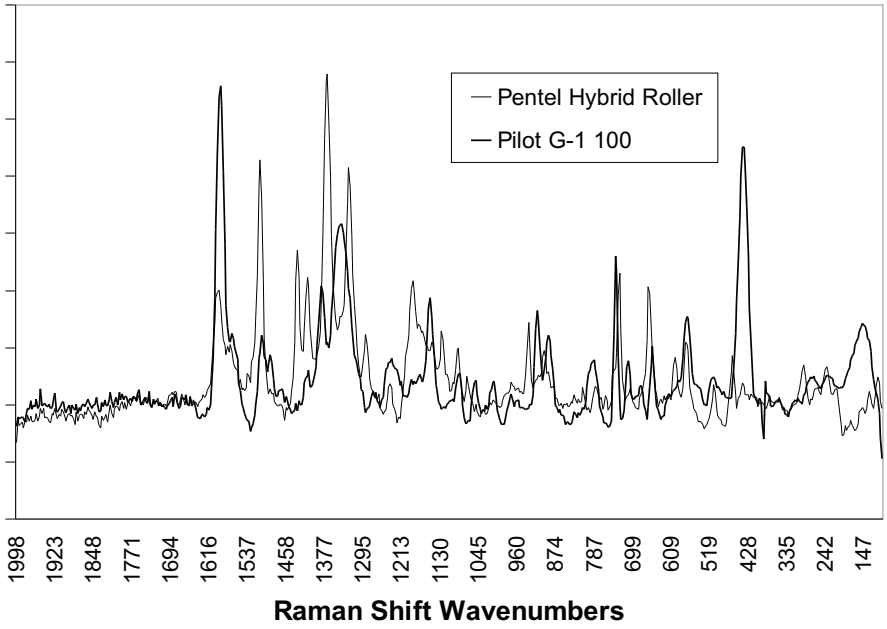

Fig. 11. Raman spectra of blue gel pen inks, Pentel Hybrid Roller (magenta), Pilot G-1 100 (blue), LabRam Infinity, SERRS 1.

The advantage of testing several sample preparation techniques is shown by comparing figures 12 and 13. Only after application of SERRS 2 the black Pilot G-1 100 gel pen shows Raman signals. The same results are obtained with the LabRam Infinity (Figure 14).

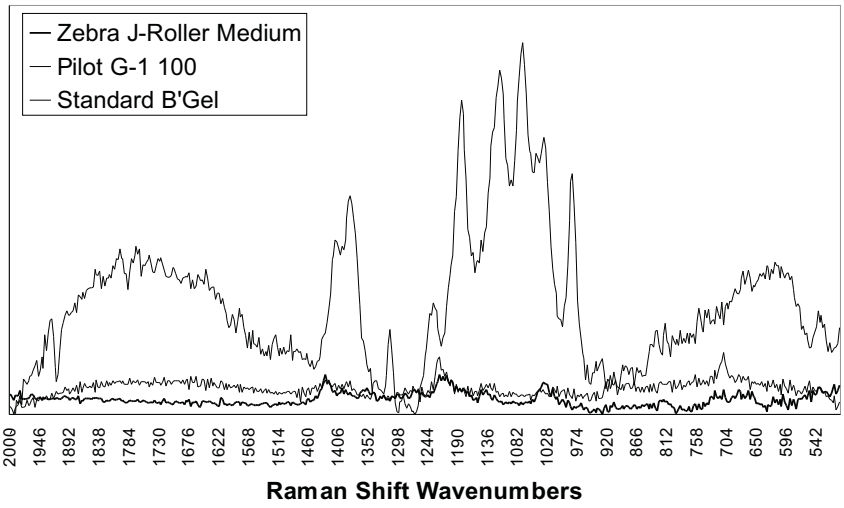

Fig. 12. Raman spectra of black gel pen inks, Zebra J-Roller Medium (blue), Standard B'Gel (red), Pilot G-1 100 (magenta), FORAM 685, SERRS 1.

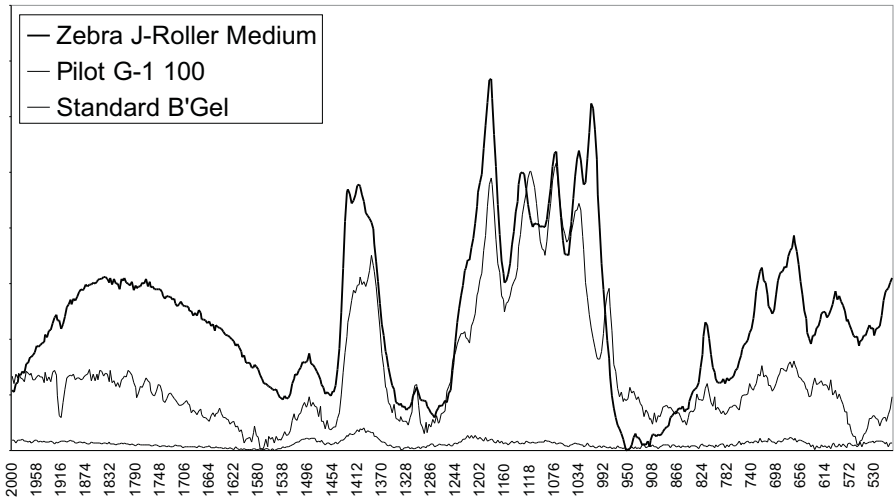

Fig. 13. Raman spectra of black gel pen inks, Zebra J-Roller Medium (blue), Standard B'Gel (red), Pilot G-1 100 (magenta), FORAM 685, SERRS 2.

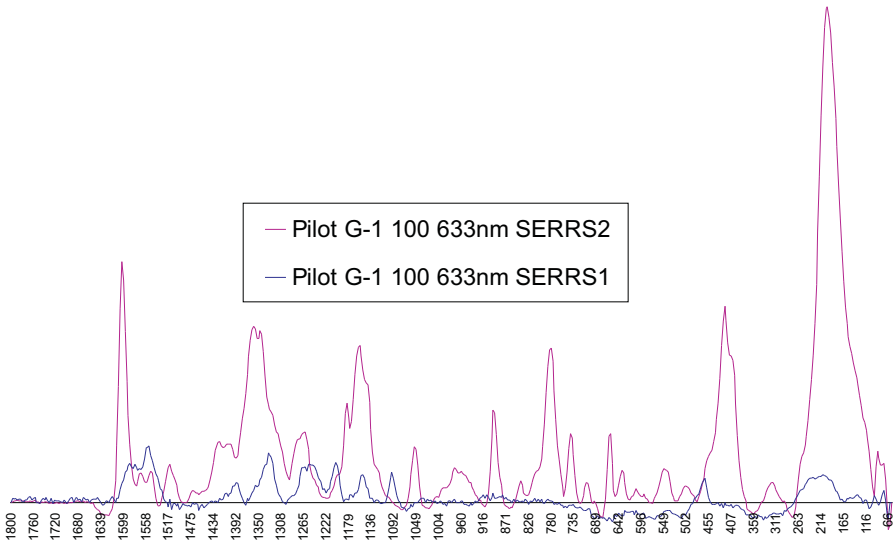

Fig. 14. Raman spectra of black gel pen ink Pilot G-1 100, SERRS 1 (blue), SERRS 2 (magenta), LabRam Infinity, ex-λ 633 nm.

CONCLUSIONS

Raman spectroscopy of inks on paper is a virtually non-destructive technique and gives additional information to "standard" methods. It should not be used as a single technique for ink examination alone, which may lead to false conclusions. Figure 15 shows two very similar spectra of a blue and a black ball point ink.

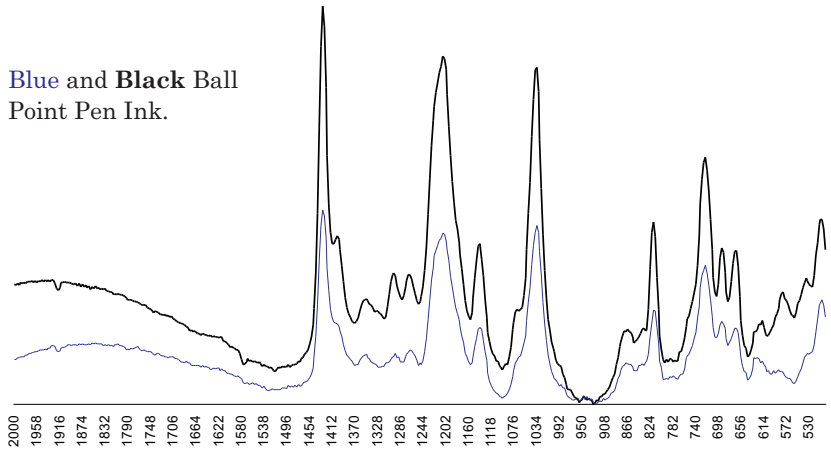

Fig. 15. Raman spectra of blue (blue) and black (black) ball point pen inks, FORAM 685, SERRS 1.

It has been shown that different sample preparation techniques and excitation wavelengths lead to different results, which may all contain valuable information. Therefore we currently cannot recommend a certain sample preparation technique or excitation wavelength but to collect and evaluate all the information taken from different techniques. Further research work is needed on Raman spectroscopy of pure ink dyes to see in which way their signals appear in ink spectra. Libraries of dyes and inks should be helpful in identification of certain ink formulations.

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References:

1. White P. C., SERRS spectroscopy – a new technique for forensic science?, *Science & Justice* 2000, vol. 40, pp. 113–119.