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The classification of ballpoint pen inks in Questioned Documents by using VSC and SERRS

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Abstract : The aim of this study was to investigate the evidential value of blue and black ballpoint pens on paper by nondestructive techniques. In this work, 21 blue and 22 black ballpoint pens which were purchased on different brands were analyzed by Raman Spectroscopy and Video Spectral Comparator (VSC). Surface-Enhanced Resonance Raman Spectroscopy (SERRS) with excitation at 685 nm and VSC with several spot light filters were used for the discrimination of ballpoint pen inks. In the SERR spectra, the ballpoint pen inks on paper could be shown sharp spectral bands and distinguished by their band shapes and relative intensities. In the blue and black ballpoint pen inks, the discriminating powers (DP) by SERRS were 0.85 and 0.67 and the DP by VSC were 0.88 and 0.90, respectively. The DP by combined sequence of techniques was all 0.97 in both black and blue ballpoint pen inks..

Key words : Forensic science, Document examination, ballpoint pen inks, SERRS

Introduction

In the questioned document examination of forensic science, one of the most important tasks is to investigate whether two or more ink entries on documents such as altered checks, money orders, legal contracts and wills have been written with the same type of ink or not.[1~3] Ball point pens are mostly the subject of forensic investigation, as most documents are completed in ink. The formula of ballpoint pen ink consists of dyes (about 45%), solvents, pigments, viscosity adjustors, and ball lubricants.[4,5] However, the composition of inks varies according to the manufacturers and brands. Numerous studies have been reported about forensic document examinations by nondestructive and destructive methods, such as Microspectrophotometry,[6~8] Thin-Layer Chromatography,[3,9] High-Performance Liquid Chromatography,[2,5,10] FTIR Spectrometry,[4] Raman Spectrometry,[11~13] Video Spectral Comparator,[10,14] Capillary Electropho- resis,[15] and Mass Spectrometry.[16,17] However, in forensic document examinations, nondestructive methods are very useful to identify of authenticity because it is very important to preserve evidences if the document is of financial or historical importance.

The luminescence (fluorescence) has been of interests in many areas of document examination and other branches of forensic science. Especially, infrared luminescence has provided a more immense value in the examination of documents than ultraviolet fluorescence. When visible light is absorbed by different inks of a similar color which are only slightly different,

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infrared luminescence can be a very big contrast between certain inks.[10,14]

Raman spectroscopy with very low power laser and charge coupled device (CCD) array detector is one of the major instruments in forensic analysis such as fibers, explosives, paints, and questioned document inks analysis. It is a nondestructive technique, so that samples can be analyzed without damage. Recently, the technique of Surface Enhanced Resonance Raman Spectroscopy (SERRS) has been reported. SERRS has been shown to be an extremely higher sensitive technique of detection without interference of the fluorescence than the traditional Raman spectroscopy. Furthermore, there are some reports that SERRS can provide the molecular structure of characterized dyes in mixtures.[11~13]

In this work, we have studied to determine the discriminating power of the blue and black ballpoint pens which were purchased in Korea and Australia by SERR spectrometry and Video Spectral Comparator, nondestructive techniques. For the further study, this work prepared a database of information on the ballpoint pen inks to compare it with multivariate chemometric strategies using principal components analysis.

Experimental

Samples

All 43 blue (21 samples) and black (22 samples) ballpoint pen inks that were targeted in this study were collected from different factories and countries or different brands of the same factory. We purchased them at stationery or supermarket in Korea and Australia. The collected blue and black ballpoint pen samples are listed in *Table* 1 and 2. The five letters in Korean were written on the ordinary A4 photocopy paper (EXP 800 Laser/copy paper, made in Indonesia) and were examined. All sheets were inserted in the new notebook and were stored inside a desk drawer within an A4 paper envelope.

Table 1. Samples of blue ballpoint pen inks

No	Brands and Models	Made in	Where buy
1	MonAmi 153 (0.7)*1	Korea	Korea
2	Barunson (desk/all 0.7)	〃	〃
3	GomuGomu	〃	〃
4	Saga eagle (Sanford-medium)	〃	Australia
5	MonAmi 153 (0.7)*2	〃	Korea
6	BiC round stic med/moy	USA	〃
7	BiC (all clear tube)	〃	〃
8	BiC diamate GRIP	Australia	Australia
9	BiC clic 2000	New Zealand	〃
10	BiC classic fine	Australia	〃
11	Presstik	India	〃
12	-	China	〃
13	Staedtler Stick 430M	-	〃
14	Artline medium	-	〃
15	BiC medium	-	〃
16	Pilot Super Grip <F>	-	〃
17	Pental B (L1.0 taiwan)	Taiwan	〃
18	Paper mate flexgrip ultra MED	-	〃
19	-	-	〃
20	Paper mate Kilometrico MED	-	〃
21	Uni Sa-S medium	Japan	〃

- : unknown information.
*1 : written in English.
*2 : written in Korean.

Instrument

1) *Video Spectral Comparator*

A high resolution video spectral comparator (VSC 2000/HR) from Foster & Freeman, Ltd was used to examine the ballpoint pen inks. The excitation lights of VSC2000/HR are produced by 250W tungsten halogen lamp for infrared luminescence with spot mode. The spectra of infrared luminescence were measured between 650 and 950 nm with different several excitation wavelengths, such as yellow green (480-620 nm), yellow (530-660 nm), reddish brown (580-700 nm), red (630- 740 nm), purple (650-750 nm) and white (400-750 nm), respectively.

2) *Raman spectrometry*

For this study we used a Foram 685 from Foster & Freeman Ltd. The Foram 685 provided the excitation wavelength of 685 nm (helium laser) and charge coupled device (CCD) for detection. The incident laser power on the sample was 4.5 mW. The spectral range was between 400 and 2000 cm^{-1} with a resolution of 8 cm^{-1}. The spot of the written letter was focused and aligned through the color video image.

Table 2. Samples of black ballpoint pens

No	Brands and Models	Manufactured	purchased
1	MonAmi 153 (0.7)[*1]	Korea	Korea
2	Barunson (desk/all)	〃	〃
3	GomuGomu	〃	〃
4	Evergreen (Nice ball 0.38)	〃	〃
5	Saga (Sanford-medium)	〃	Australia
6	MonAmi 153 (0.7)[*2]	〃	Korea
7	BiC round stic med/moy	USA	〃
8	BiC N-S medium france design	〃	〃
9	BiC (all clear tube)	〃	〃
10	BiC diamate GRIP	Australia	Australia
11	BiC clic 2000	New Zealand	〃
12	BiC classic fine	Australia	〃
13	Presstik	India	〃
14	-	China	〃
15	BiC Cristal M	-	〃
16	Artline medium	-	〃
17	Pental BK (L1.0) taiwan	Taiwan	〃
18	-	-	〃
19	Pilot Super Grip <M>	-	〃
20	Paper mate Kilometrico med PT	-	〃
21	Staedtler Stick 430M	-	〃
22	Uni Sa-S medium	Japan	〃

- : unknown information.
[*1] : written in English.
[*2] : written in Korean.

Chemicals

Poly (L-lysine) solution (0.01%, MW 70,000 - 150,000) was purchased from Sigma-Aldrich (USA). The Silver Colloid was obtained from British Biocell International Ltd (BBInternational).

Sample procedures

For SERR spectra we applied silver colloid solution on written letter. 0.2μL of a poly (L-lysine) solution was added on the spot of the written letter. After drying the silver colloidal solution (0.2 μL) was applied on the same spot. The Raman spectrum was recorded within 2 min after treating the sample. Five SERR spectra were obtained for each ink sample.

Discriminating power

The discriminating power (DP) of the different brands for ballpoint pens was defined as the ratio of the number of discriminated pairs to the number of possible pairs.[3,18]

$$DP = \frac{\text{Number of discriminated pairs}}{\text{Number of possible pairs}}$$

The number of total possible pairs (for example, 210 and 231 in blue and black ballpoint pen inks, respectively) and discriminated pairs were counted among ballpoint pen inks.

Results and Discussion

Infrared luminescence with video techniques is commonly examined for its nondestructive property in forensic ink analysis. Differences in luminescence of inks were dependent on variations of visible wavelength of the exciting light, such as yellow green, yellow, reddish brown, red, purple, and white. The resultant luminescence was detected by sensitive video camera (VSC/HR). All of the letters were written on the same paper and tested infrared luminescence.

As it was shown in *Fig*. 1~5, luminescence of some ballpoint pen inks in the infrared region appeared, not in others. A further variation was shown in both their intensity and the different excitation wavelength. The seven kinds of inks showed strong luminescences at yellow green wavelength of the excitation radiation in both black and blue ballpoint pen inks (for example, the written letter K13, K31 in black and E33 in blue ball point pen inks of *Fig*. 1 and 3, respectively). As can be seen in *Fig*. 1 and 2, the Presstik black ballpoint pen (made in India, the written letter K51) and the black ballpoint pen which was made in China (no brand information, the written letter K52) showed weak

Fig. 1. Black inks photographed in yellow green wavelength of the exciting radiation.

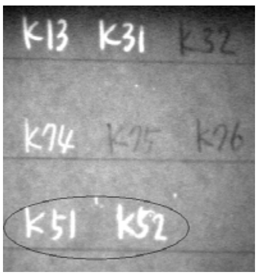

Fig. 2. Black inks photographed in yellow wavelength of the exciting radiation.

luminescences (shown as both dark and bright) at yellow green wavelength of the excitation, however, they exhibited strong luminescences at yellow wavelength of the excitation. In the blue ballpoint pen inks a Papermate ballpoint pen ink (purchased in Australia) did not show its luminescence at yellow green excitation wavelength (the written letter E78 in *Fig*. 3). However, it began to show its luminescence dimly when an excitation wavelength

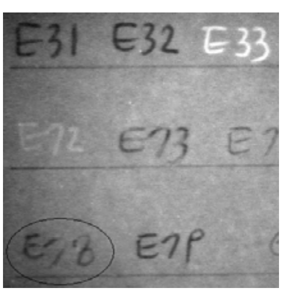

Fig. 3. Blue inks photographed in yellow green wavelength of the exciting radiation.

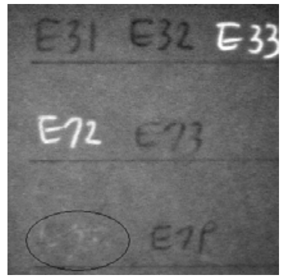

Fig. 4. Blue inks photographed in reddish brown wavelength of the exciting radiation.

was changed to reddish brown from yellow wavelength, and further showed a weak luminescence at red excitation wavelength (the written letter E78 in *Fig*. 3, 4, and 5).

The classification of the inks on the same background according to the VSC/HR was based on comparison of their resultant luminescence *i.e.* whether the luminescence appeared or not, the exciting wavelength range at which the luminescence appeared, and their intensity. Furthermore, the line width of written letter was discriminated in sensitive video camera of VSC. Therefore the line width was used to classify the ballpoint pen inks.

Fig. 5. Blue inks photographed in red wavelength of the exciting radiation.

The discriminating powers of both infrared luminescence and line width were calculated as 0.90 and 0.88 for black and blue ballpoint inks, respectively. However, the discriminating powers of only infrared luminescence (excluding line width) were found to be 0.74 and 0.80 for black and blue ballpoint pen inks, respectively (*Table* 3).

Table 3. Discriminating power of the individual and combined techniques

techniques	ballpoint pen inks	
	blue	black
infrared-luminescence (exclude line width)	0.80	0.74
infrared-luminescence (include line width)	0.88	0.90
SERRS	0.85	0.67
combined sequence	0.97	0.97

SERR spectra of the inks entries were obtained *in situ*, by using the helium laser as excitation wavelength of 685 nm. *Fig.* 6 showed two spectra of blue ballpoint pen ink (Pental B, made in Taiwan) with and without the treatment of silver sol colloidal solution. As can be seen, SERR spectrum of a blue ink with silver colloidal solution showed sharp spectral Raman bands, while the spectrum without the of colloidal solution did not show any Raman band. The SERRS depended on both the strength of interaction between particular dye molecule (cationic charged) and a negatively charged silver sol particle, and the resonance effect at the applied excitation wavelength.

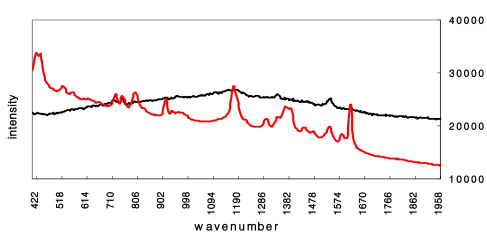

Fig. 6. SERR spectra of blue ballpoint pen inks (sample number is 17, Pental B, made in Taiwan). The black line is without the treatment of silver sol colloidal solution, and the red line is with the treatment of silver colloidal solution.

Fig. 7 and 8 showed the SERR spectra for both blue and black inks. Specific Raman bands were observed to be discriminated between the different brands inks. Average spectrum was obtained from five spectra of each ink samples at the different position in the same sample letter.

The following criteria were used to classify the ballpoint pen inks according to the SERRS, *i.e.* whether the Raman bands were represented or not (considering differences of more than 10 cm^{-1} as significant), the relative intensities of the two sharpest bands in the 1550~1650 cm^{-1} (considering differences of more than 5% as significant), and whether some spectral band shift occurred or not.[11] For instance, as shown in *Fig.* 7 the SERR spectra of sample number 5 and 18 looked very similar but some spectral shift of sample number 18 in the near 1190 cm^{-1} region appeared, and their relative intensities of the two sharpest bands were different.

Finally, the blue ballpoint pens were classified into eleven groups. In detail, the relative intensities of the two sharpest bands in the 1550 ~ 1650 cm^{-1} region were 0.8, 5.3, 0.3, 1.1, 7.6, 0.4, 0.1, and 0.6 in the blue samples. First of all, blue samples were classified into 8 groups. And another group did not show any peak in both the SERR and Raman spectrum. The relative intensities of two groups (for example actually, 0.31 and 0.34 in the sample number 8 and 17, respectively) were

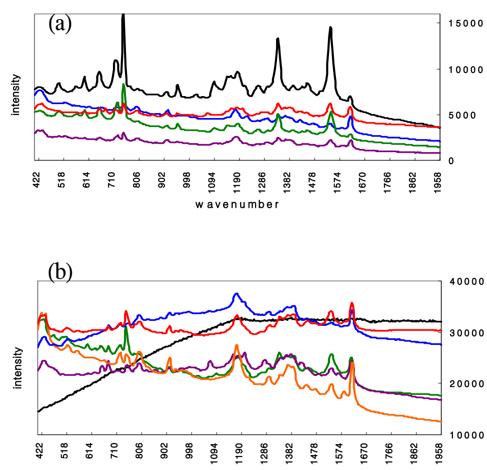

Fig. 7. SERR spectra of blue ballpoint pen inks. a) the violet, green, blue, red, and black lines are sample number 5, 9, 8, 18, and 15, respectively. b) the orange, violet, green, blue, red, and black lines are sample number 17, 16, 21, 14, 20, and

13, respectively and refer to *Table* 1.

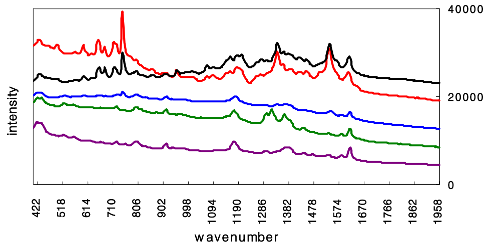

Fig. 8. SERR spectra of black ballpoint pen inks. The violet, green, blue, red, and black lines are sample number 16, 22, 14, 15, and 11, respectively and refer to *Table* 2.

the same as 0.3, however, due to their different spectral shapes in the 1050～1250 cm^{-1} regions, both inks were classified into two groups. The relative intensity of the sample number 5 and 21 were equal as 0.85 but the sample number 21 was classified as different from the sample number 5 because of their different specific shapes in the 1300～1400 cm^{-1} regions.

The black ballpoint pen inks classified into five groups (*Fig*. 8). Unfortunately, the eleven kinds of ball point pen inks showed similar SERR spectra (violet line in *Fig*. 8) and belonged to the same group. The second group contained also seven kinds of ball point pen inks (their SERR spectrum was blue line in *Fig*. 8). In case of black inks, several kinds of ball point pen inks showed very similar spectrum pattern (for example, the first and second groups were contained eleven and seven kinds of ball point pen inks, respectively), because the observed scattering from CV is weak because resonance plays no role at 685 nm, while the scattering of solvent blue 38 (mostly contained in blue ballpoint pen inks) is considerably intensified by resonance at this wavelength.

The discriminating powers of SERRS were 0.85 for the blue inks and 0.67 for the black inks. The discriminating power in the blue inks was larger than the DP in the black inks. *Table* 3 showed the discriminating power of both individual and combined techniques. In the individual technique, the black inks had the highest discriminating power (0.90) with VSC/HR technique and the worst discriminating power (0.67) with SERRS technique. However, in the combined techniques, the discriminating power was 0.97 for both blue and black inks.

The large values of discriminating power for black and blue inks in the combined techniques mean that authenticity can be distinguished in the questioned document by only nondestructive techniques.

Conclusion

The twenty one blue and twenty two black ballpoint pens with different brands were analyzed by using both VSC and SERRS techniques which is nondestructive for forensic ink examination. The blue inks had a better degree of discrimination than the black inks by SERRS. In the blue and black ballpoint pen inks, the DPs by SERRS were 0.85 and 0.67 and the DPs by VSC were 0.88 and 0.90, respectively. The DP by combined sequence of techniques was all 0.97 in both black and blue ballpoint pen inks.

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