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The Classification and Age Determination of Ballpoint Pen Inks in Questioned Documents

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Abstract : The aim of this study was to investigate questioned documents written with blue or black ballpoint pen on paper by nondestructive technique. In this work, 21 blue and 22 black ballpoint pen inks which were purchased on different brands were analyzed by using Microspectrophotometry (MSP). The reflectance spectra were obtained from these ink samples and their shapes and the wavelength of the maximum intensity were compared. In the blue and black ballpoint pen inks, the discriminating powers (DP) were 0.85 and 0.61, respectively. The changes of the reflectance intensity at their wavelength of maximum intensity and their shapes appeared according to the exposure time to sunshine in a laboratory, especially in the blue ballpoint pen inks. Therefore it is possible to distinguish ink entries on the same paper with the relative age in case of questioned letters written with blue ballpoint pen.

Key words : Forensic science, Document examination, inks, ageing, MSP

Introduction

Microspectrophotometry (MSP) has been widely used in forensic science to identify paints, inks, and fibers.[1~5] In those forensic evidences, it is an important nondestructive technique for the comparison of coloured materials. Reflectance measurements can not only accurately describe the dyes or pigments colour, but can be used for colour matching and differentiation as well. In forensic ink examination, MSP assists the document examiners to investigate the authenticity of questioned documents in comparison with the similarity between two or more written ink entries on questioned documents in cases that these inks have different qualitative composition or differences in relative propositions' their same components.

The ballpoint pen ink consists of dyes (about 45%), solvents, pigments, viscosity adjustors, and ball lubricants. However, the composition of inks may be very various according to the manufacturers and brands.[6,7] These components undergo slow chemical changes due to storage conditions, such as light, temperature and humidity, and period. As soon as the ink is placed on a paper, the inks solvents start to evaporate intensively and then chemical processes such as, aerial oxidation, cross-linking and hydrolysis are made slowly, at more or less steady rates. These degradations depend on the storage condition of documents. And determining the age of ballpoint pen ink is a very difficult in questioned document examination.[8,9]

Several nondestructive and destructive analytical instruments have been used in the examination of

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ballpoint pen ink on paper such as, MSP,[2,10,11] Thin-Layer Chromatography,[3,12] High-Performance Liquid Chromatography,[7,13,14] FTIR Spectrometry,[6] Raman Spectrometry,[15~17] Video Spectral Comparator,[14,18] Capillary Electrophoresis,[19] and Mass Spectrometry.[20,21] Especially, in forensic document examinations, nondestructive methods are very useful for identification of authenticity and important in aspect of preservation of evidences if the document is of financial or historical importance.

Nowadays, some authors have tried to prepare the database or pattern recognition of information on ballpoint pen inks because it is very useful to identify the ballpoint pens manufactures or the specification of ink written on the questioned documents.

In this work, we have studied to determine the discriminating power and the relative age of the blue and black ballpoint pen inks which were purchased in Korea and Australia by MSP. For the more study, this work was prepared as a database of information on the ballpoint pen inks for comparing with multivariate chemometric strategies using principal components analysis.

Experimental

Samples

All 43 blue (21) and black (22) ballpoint pen inks that were targeted in this study were collected from different factories and countries or different brands of the same factory. We bought them at stationery or supermarket in Korea and Australia. The collected blue and black samples are listed in *Table* 1 and 2. The five letters of 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.

A series of the ageing document samples were exposed to sunshine inside a laboratory (room temperature: about 20~23 ℃), close to the windows, up to 6 weeks. Usually, samples were exposed to sunshine through the window in the morning (for about 4 hours) directly. Another series of the aging sample was kept in a rear cotton trousers pocket folded in four in summer. This sample was kept up to 16 weeks and sometimes, exposed to a little bit sweat.

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.

Instruments

The instrument used was a Rofin Microcolourite/BH-2 Olympus microspectrophotometer with reflection mode. The intensity of reflectance (%) was measured between 400 and 740 nm of wavelength with 50 scan per measurement of each of the inks. The average spectrum was obtained from five spectra for each ballpoint pen ink.

All spots of each letter for analysis were placed avoiding the bronzed area in the field of vision of the

Table 2. Samples of black ballpoint pens

No	Brands and Models	Made in	Where buy
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.

microscope because the bronzing effect of inks on paper may interfere substantially in the reproducibility of their reflectance spectra. letter spots that look apparently similar in thickness and surface characteristics were chosen.

Discriminating power

The discriminating powers (DP) of the different brands for ballpoint pens were calculated according to the formula (Smalldon and Moffat),[3,22] that the number of total possible pairs (for example, 210 and 231 in blue and black ballpoint pen inks, respectively) and discriminated pairs among ballpoint pen inks were counted, and divided the number of discriminated pairs by the number of total possible pairs.

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

Results and Discussion

A reflectance microspectrophotometer measures colour by illuminating an ink line with the visible wavelengths and the amount of light reflected. Since the colour of an ink is due to the particular dyes and pigments, the spectrum should be distinctive, and unique to that particular dye combination.

All of the spectra were obtained without bronzing interferences. A slight difference in the reflectance intensity among the five spectra for any of the individual inks was shown but there was no shift in wavelength. The average spectrum from the five spectra for each inks was compared to classify among the same colour ballpoint pen inks.

As can be seen in *Fig.* 1 and 2, 21 blue and 22 black ballpoint pen inks were classified into seven and five groups, respectively, according to their spectral characteristics.

In blue ballpoint pen inks (*Fig.* 1), the spectrum of MonAmi 153 (sample number 5, made in Korea) showed two maximum reflectance intensities at 467 and 648 nm and it increased steeply from 697 nm. The spectral curve of BiC (sample number 7, made in USA) showed a maximum reflectance intensity at 451 nm, and increased steeply from 693nm. However, in Staedtler Stick 430 M (sample number 13), its maximum reflectance intensity appeared at 458 nm and the spectral curve increased slowly from 630 nm.

In black ballpoint pen inks (*Fig.* 2), the maximum reflectance intensity did not appear prominently but very weakly in a few samples. The spectrum of Saga (sample number 5, made in Korea) showed that the curve decreased from 400 nm to 437 nm, and then increased very slowly to 740 nm, and there was no maximum reflectance intensity. The spectrum of Artline

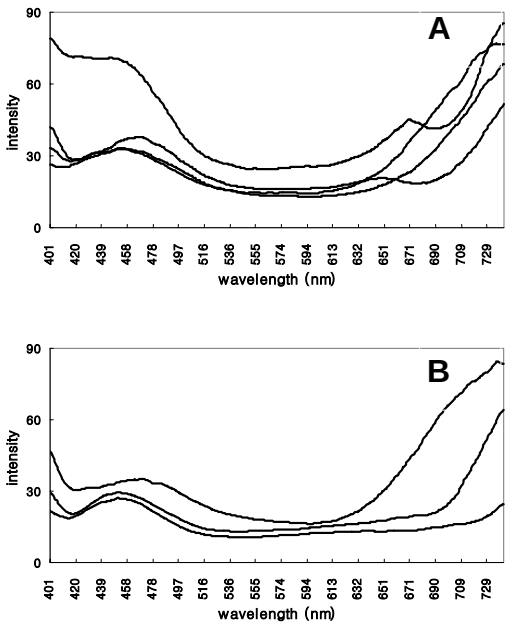


Fig. 1. MSP spectra of blue ballpoint pen inks. A: The sample numbers from bottom are 5, 13, 12, and 11, at 709 nm. B: 21, 7, and 19 and refer to *Table* 1.

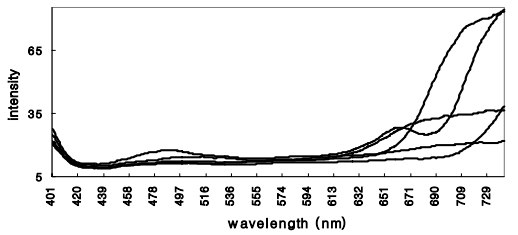


Fig. 2. MSP spectra of black ballpoint pen inks. The sample numbers from bottom are 11, 5, 4, 16, and 14 at 660 nm and refer to *Table* 2.

medium (sample number 16) showed the maximum intensity from 471 nm to 519 nm, but it was very weak as shown in *Fig*. 2. The spectrum of BiC clic 2000 (sample number 11, made in New Zealand) showed very weak maximum reflectance intensity at 493 nm, and increased from 699 nm very steeply.

The discriminating powers by MSP were calculated according to the formula in Experimental section, and shown in *Table* 3. The discriminating powers were 0.85 and 0.61 in blue and black ballpoint pen inks, respectively.

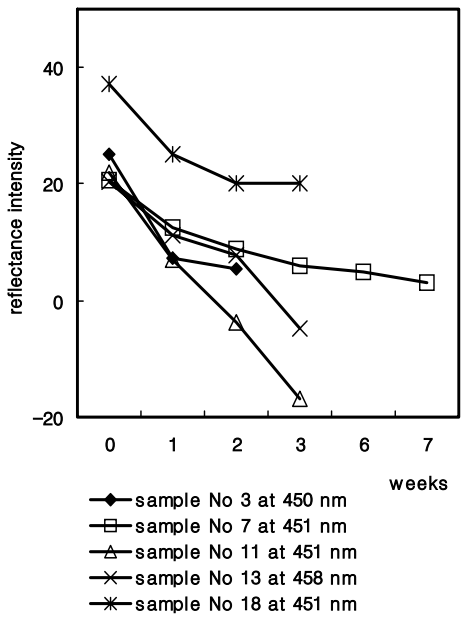
Table 3. Discriminating power by the MSP

techniques	ballpoint pen inks	
	blue	black
MSP	0.85	0.61

The blue ballpoint pen inks had a greater discriminating power than the black ballpoint pen inks. It provides a higher probability in identifying questioned document written in the blue inks than in the black inks on the same paper by MSP.

Reflectance microspectrophotometer for estimating the relative age of letter written with ballpoint pen inks had been used. Samples were made by writing letters with blue ballpoint pens in A4 photocopy paper, and then were exposed to sunshine inside a laboratory, close to the windows, up to 7 weeks. As it was shown in *Fig*. 1, blue inks have a maximum point of reflectance between 415 nm and 480 nm and a minimum between 500 nm and 650 nm.

The reflectance spectra were normalized by subtracting minimum intensity from intensity at each wavelength for comparing their intensities depended on age. *Fig*. 3 showed the intensities at the maximum reflectance wavelength of the fresh samples according to the age. In all kinds of blue ballpoint pen inks, the intensity at the maximum reflectance wavelength of the fresh samples (this letters were not exposed to the sunshine) decreased depending on the exposure time (*Fig*. 3). Ballpoint pen inks contain various dyes, solvents, and additives, but different composition according to the manufactures, brands or models, even batches. As an ink fades with time on paper, solvents evaporate, resins polymerize and dyes degrade. Therefore the spectra with maximum intensity and wavelength would be affected by solvent evaporation or dyes oxidation of inks. Simultaneously, most of maximum points shifted to longer wavelengths (*Fig*. 4)



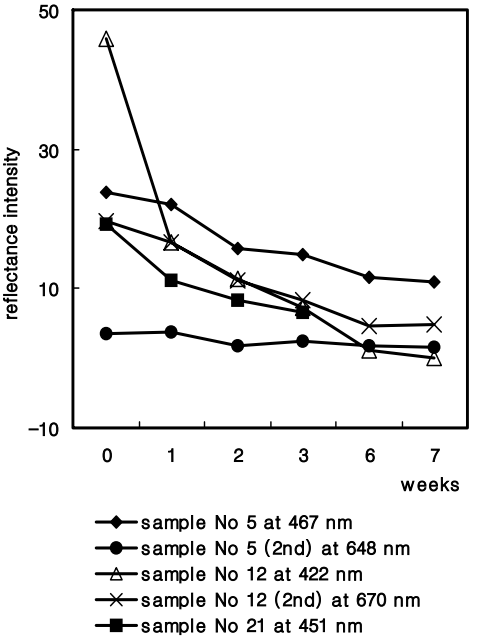


Fig. 3. The change of intensities at the maximum reflectance wavelength of the fresh samples with age. The sample letter written with blue ballpoint pens was exposed to sunshine for 0, 1, 2, 3, 6, and 7 weeks.
(2nd) : second maximum.

with age except those of the blue ballpoint pen inks (sample number 18 and 21) (*Fig.* 4).

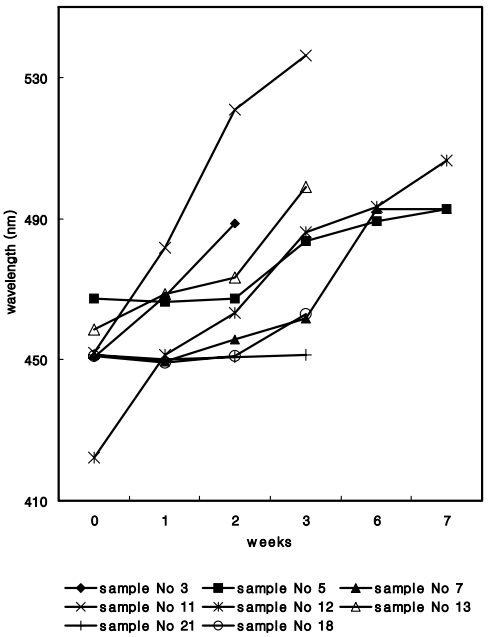


Fig. 4. The change of the maximum reflectance wavelength with age. The sample letter written with blue ballpoint pens was exposed to sunshine for 0 to 7 weeks.

Four kinds of blue ballpoint pen inks that were sample numbers 1, 5, 12, and 15 had the second maximum and minimum points from 630 nm to 680 nm and 670 nm to 700 nm, respectively. The blue ink (sample number 12) appeared to decrease its intensity at the second maximum reflectance wavelength of the fresh sample (670 nm) with age (*Fig.* 3). However, the second maximum reflectance wavelength shifted slightly to a shorter wavelength.

The sample numbers 1, 5, and 15 blue inks did not show any change of their second maximum intensity and wavelength, promptly.

However, the black ballpoint pen inks showed very different results with age.

As it was shown in *Fig.* 5 and 6, the change of the reflectance intensity at the maximum reflectance

wavelength of the fresh samples did not appear promptly, even though the written letters were exposed to sunshine up to 7 weeks. Only the sample number 14 (made in China) black ballpoint pen ink showed a small change that the second maximum intensity of 664 nm increased with the exposure time (*Fig.* 7).

It can provide information - whether two or more ink entries on document have been written in the same time or not in case of forgery written with the blue ballpoint pens. That means it is possible to distinguish ink entries on the same paper according to the relative age.

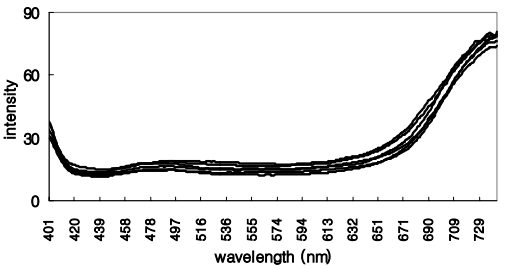


Fig. 5. The spectra of the reflectance intensity according to the ageing. The sample letter written with MonAmi 153 black ballpoint pen (sample number 6) was exposed to sunshine for 0, 1, 2, 3, 6, and 7 weeks.

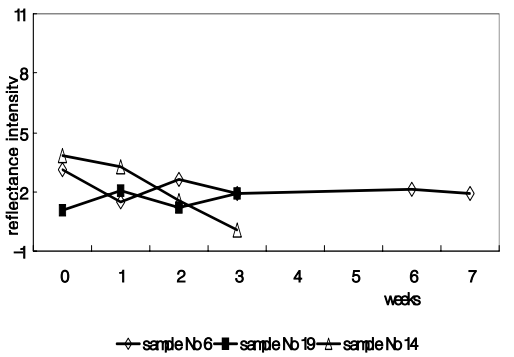


Fig. 6. The change of intensities at the maximum reflectance wavelength of their fresh samples with age. The sample letter written with black ballpoint pens was exposed to sunshine for 0 to 7 weeks.

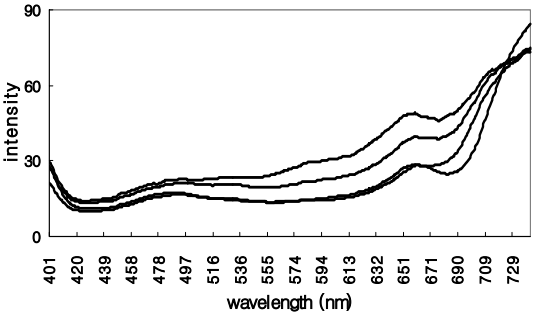


Fig. 7. The spectra of the reflectance intensity according to the ageing. The sample letter written with sample number 14 black ballpoint pen (made in China, no information of brand name) was exposed to sunshine for 0, 1, 2, and 3 weeks.

We tried to examine the changes according to sweat, folding, and age without sunshine. Lots of letters, documents, or memo were kept in the pocket of the clothes carelessly. We thought the fading could be very slow in this keeping condition. *Fig.* 8 and 9 showed the spectra of the reflectance for Barunson blue (sample number 2) and the sample number 14 black ballpoint pen inks while the letters written with those pens were kept in the rear cotton trousers pocket for 16 weeks. The spectrum change of the reflectance by MSP did not appear in both blue and black inks. Under this condition, it was difficult to observe significant changes among the different inks by MSP only.

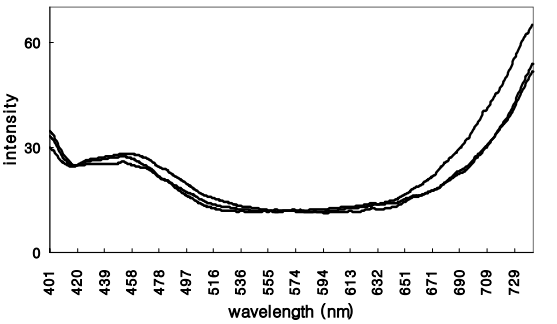


Fig. 8. The spectra of the reflectance intensity according to the ageing. The sample letter written with Barunson blue ballpoint pen (sample number 2) was kept in the rear pocket of jeans for 0, 5, and 16 weeks.

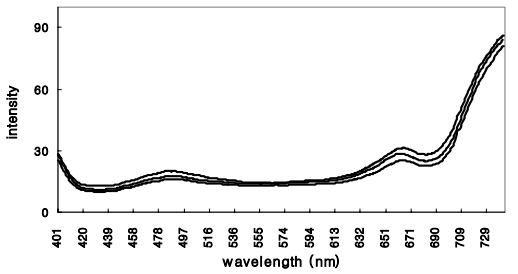


Fig. 9. The spectra of the reflectance intensity according to the ageing. The sample letter written with sample number 14 black ballpoint pen (made in China, no information of brand name) was kept in the rear pocket of jeans for 0, 5, and 16 weeks.

Conclusion

The forty three blue (21) and black (22) ballpoint pen inks of different brands were analyzed by using MSP (nondestructive technique) for forensic examination of inks. The blue inks had a greater discriminating power than the black inks. The discriminating powers were 0.85 and 0.61 in the blue and black ballpoint pen inks, respectively.

The reflectance spectra showed the changes of the inks according to the fading to the sunshine in the blue inks. That represents it is possible to distinguish ink entries on the same paper with the relative age.

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