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Systematic Analysis of Bulk Blue Ballpoint Pen Ink by FTIR Spectrometry

ABSTRACT: A classifying method on bulk blue ballpoint pen ink has been studied by Fourier transform infrared (FTIR) spectroscopy. By using this method, a total of 108 blue ink samples have been divided into two groups depending on their main component. Spectral characteristics of these inks such as frequency and absorbance are described by way of artificial intelligence of pattern recognition, and 35 subgroups from the 108 inks are distinguished by their correlation coefficient (λ). Under heat or exposure to ultraviolet light a mode of change in the age of the inks has been obtained. This approach has provided a reliable and nondestructive method for the characterization of bulk ballpoint writing ink, and more importantly, it might be a basis for dating of the blue ballpoint pen ink.

KEYWORDS: forensic science, ballpoint writing inks, FTIR spectrometry, nondestructive analysis, artificial intelligence, pattern recognition

Determining the type and age of ballpoint ink is a difficult and challenging subject in forensic science (1–3). The formula for ballpoint ink generally consists of dyes, solvents, resins, viscosity adjustors, and ball lubricants, etc. However, the ink composition may vary from one manufacturer to another. Cantu found that a relationship exists between the age of ballpoint ink and the rate in which ink can be extracted from paper using weak solvents (4). Lyter, Shoji, and Xu have analyzed the ballpoint inks on paper by TLC, HPLC, and MECC (5–7). In 1985, Stewart reported a gas chromatography procedure for comparing the relative ages of ballpoint inks on paper (8). FTIR spectroscopy has been widely used in forensic science to analyze a variety of evidence (9,10). Merrill, Bartick (1), and Harris (11) concluded that diffuse reflectance (DR) FTIR might be a viable method for nondestructive analysis of ink on paper. However, the spectra of ink on paper that Harris obtained did not compare with their reference spectra of the inks themselves (11). Humecki found changes in the hydroxyl (OH) and carbonyl (CO) infrared absorption bands as ink aged. His observations were limited to just one ballpoint ink formulation (12).

One hundred and eight samples of blue ink, made in China, were collected and analyzed by FTIR spectroscopy. These spectra were associated with the chemical components of the inks and were divided into two groups. The spectra data of these inks, such as peak location and peak intensity, were described and summed up by an artificial intelligence of pattern recognition, and 35 subgroups of the two groups were obtained on the basis of their correlation coefficient (λ). A kinetic examination was carried out by heating the samples or exposure the samples to ultraviolet light. Each sample's spectrum was obtained according to the time of heating or exposure, to study the chemical component's change mechanism by using the spectrum curve fitting method. We obtained the changed peak height ratio relation with time.

In comparison with the traditional approaches such as chromatographic, normal spectrophotometer, and solvent-extracted methods, the advantage of this method is that it is fast, reliable, and nondestructive (13–15); however, the method must be further tested on inks applied to paper.

Materials and Methods

Sample Collection

All 108 blue ballpoint pen samples were collected from different factories in China or are different brands of the same factory. They were stored on KBr plates directly for obtaining FTIR spectra. The sample inks were chosen without the knowledge of their chemical formulation.

Equipment and Software

A Perkin-Elmer Spectrum 2000 FTIR Spectrometer and Auto Image Microscope and a narrow band MCT (mercury cadmium telluride) detector were used to collect the FTIR spectra. The instrument was operated at 8 cm^{-1} resolution over a spectral range of 4000 to 700 wavenumbers (cm^{-1}). The number of scans is 50, OPD velocity is 2 cm/s, and gain is 1. The wavelength of a UV lamp (Shanghai Keyi Optical Factory, Shanghai, China) is 254 nm. We used self-programmed BBP-FTIR software.

Methods

The FTIR spectra of 108 kinds of ballpoint pen inks (three times per sample) were obtained and transformed into ASCII form. In pattern recognition, the same peak location (jcm^{-1}) was chosen in two comparison spectra. The correlation coefficient (λ) of the two spectra was calculated by the following expression:

$$\lambda = \frac{\sum W_j A_j B_j}{(\sum W_j A_j A_j)^{1/2}(\sum W_j B_j B_j)^{1/2}} \tag{1}$$

where A_j and B_j are the absorbance in spectra A and B at frequency j, and W_j is a weighting that depends on the filters selected (the fil-

ters are used to eliminate the influence of wavenumber, the resolution, intensity, noise, and CO$_2$). The spectral comparison range is 4000 to 700 cm^{-1}, which is continuous.

After the reference spectrum was determined, FTIR spectra of all inks were depicted and resolved based on the following program frame (Fig. 1), and classified by their correlation coefficient (λ). The factories, brands, and lot numbers could be inferred.
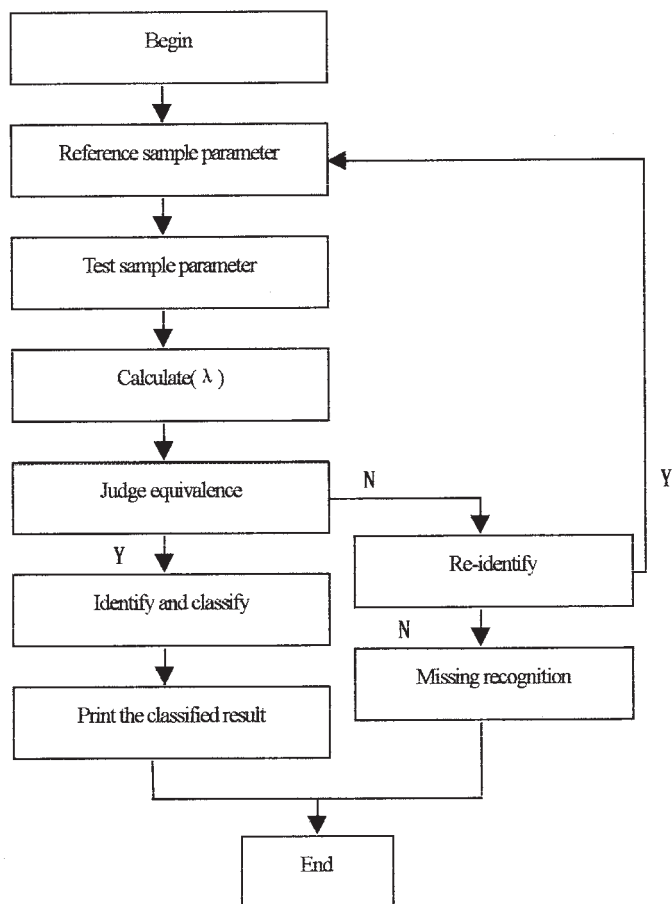

FIG. 1—*The program frame of pattern recognition.*

Results and Discussion

Ink Spectra

The 108 ink samples could be classified into two groups according to their spectral characteristic. In the first group, there was no peak shown in the range from 2000 to 1700 cm^{-1}, which is the characteristic frequency of carbonyl (C=O) stretching vibration. This means that there were no aliphatic acid or their esters present. The spectrum of sample 46 was shown in Fig. 2a. The peak at 1584, 1360, and 1176 cm^{-1} belonged to the characteristic absorption of triarylmethane dyes. The peak at 1245 cm^{-1} can be assigned to the vibration of aromatic ether (Ar—O), and the absorption bands at 1296, 1094, and 1055 cm^{-1} reflected the asymmetrical and symmetrical stretch vibration of aliphatic ether (C—O). Moreover, the absorption band at 914 cm^{-1} was caused by terminal epoxy bond, and 832 cm^{-1} was from the out-of-plane bending of the two adjacent hydrogen at p-substituted benzene ring.

It should be noticed that most of the absorption bands in the ink spectra are complex peaks. For example, in the above-mentioned spectra, the stretch vibration of an unsaturated C—H bond and the asymmetrical vibration of —CH$_2$ in the epoxy resin caused the absorption band at 3062 cm^{-1}. (In cyclic compounds, as the cyclic tension and the extent of sp^2 hybrid increased, the stretch vibration of —CH$_2$ will be shifted to high frequency.) Meanwhile the absorption band at 1584 cm^{-1} contained the skeletal vibration of triarylmethane dye and the C=C stretch vibration of epoxy resin (about 1581 cm^{-1}). The absorption frequency at 1360 cm^{-1} also contains the symmetrical bending vibration. The analysis results showed triarylmethane dyes, the epoxy resin, and the solvents existed in the first group of inks.

In the second group, there was a strong absorption band of carbonyl (C=O) from 2000 to 1700 cm^{-1}. The spectrum of sample 96 was shown in Fig. 2b. According to the strong carbonyl (C=O) absorption band at 1730 cm^{-1} and the asymmetrical and symmetrical stretch vibration of the C—O—C bonds at 1285, 1126, and 1073 cm^{-1}; the presence of ester could be confirmed. The spectrum also indicated that the main component in this kind of ink was alkyd resin. On the contrary, the absorption bands of the triarylmethane dyes were inconspicuous.

It is obvious that the blue ballpoint pen ink is a mixture of dyes such as triarylmethane dyes, epoxy resin, alkyd resin, and solvents, etc.
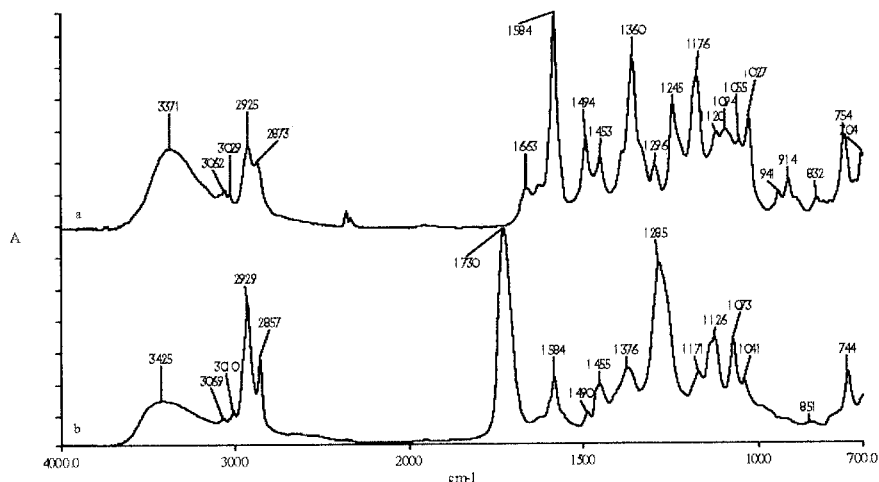

FIG. 2—*FTIR spectra of the ink test sample 46 (a) and 96 (b).*

Pattern Recognition

In pattern recognition, the first step is to obtain three spectra of an ink sample, then to assess the quality of the spectra and to select the best spectrum; the next step is to pick out 35 spectra as the reference spectra for comparison with the test spectra of the other 73 ink samples. Once a reference spectrum was chosen, the other spectra could be compared to it. According to the calculated correlation coefficient (λ), they were further divided into corresponding subgroups. For example, there are 14 samples in the first group. The spectra with correlation coefficient (λ) above 0.9800 were generally considered as the same species. When λ value was lower than 0.9800, it needed to choose a new reference spectrum to resume. Then all 108 samples were classified into 35 subgroups with 6 subgroups in the first group (I) and 29 subgroups in the second group (II).

Table 1 shows the pattern recognized procedure, a part of the spectra from the first group (I) and test samples 96 and 39 from the second group (II) were selected to be compared to the reference sample 46, 41, 11, 51, and 8. When reference sample 46 was chosen as the reference spectrum for comparison, the correlation coefficient (λ) of the three spectra of test sample 45 were all above 0.9800, so samples test 45 and 46 could be considered as the same subgroup in the first group. Other samples which had lower λ compared with 46 needed to choose a new reference spectrum to dis-

TABLE 1—*The correlation coefficient (λ) of a part of the spectra in the first group inks (I) and test samples 96, 39 (II).*

Test Sample	Reference Sample				
	46	41	11	51	8
2 (I)	0.9674	0.9827	0.9257	0.9432	0.9777
	0.9477	0.9518	0.9039	0.9328	0.9587
	0.9280	0.9293	0.8651	0.8854	0.9188
8 (I)	0.9746	0.9737	0.9425	0.9560	1.0000
	0.9718	0.9719	0.9373	0.9487	0.9921
	0.9639	0.9706	0.9293	0.9471	0.9879
10 (I)	0.9740	0.9849	0.9903	0.9620	0.9935
	0.9618	0.9678	0.9695	0.9382	0.9885
	0.9236	0.9114	0.9442	0.8828	0.9495
11 (I)	0.9426	0.9539	1.0000	…	…
	0.9345	0.9390	0.9982	…	…
	0.9281	0.9314	0.9945	…	…
13 (I)	0.9738	0.9992	…	…	…
	0.9693	0.9967	…	…	…
	0.9531	0.9745	…	…	…
16 (I)	0.9766	0.9909	…	…	…
	0.9690	0.9850	…	…	…
	0.9689	0.9809	…	…	…
39 (II)	0.7193	0.7108	0.7396	0.7656	0.7252
	0.7172	0.7104	0.7385	0.7650	0.7226
	0.7109	0.7053	0.7325	0.7607	0.7204
41 (I)	0.9774	1.0000	…	…	…
	0.9766	0.9971	…	…	…
	0.9733	0.9968	…	…	…
45 (I)	0.9921	…	…	…	…
	0.9906	…	…	…	…
	0.9893	…	…	…	…
46 (I)	1.0000	…	…	…	…
	0.9985	…	…	…	…
	0.9978	…	…	…	…
51 (I)	0.9568	0.9716	0.9179	1.0000	…
	0.9503	0.9659	0.9116	0.9982	…
	0.9471	0.9635	0.9032	0.9921	…
96 (II)	0.4531	0.4254	0.5387	0.4689	0.4671
	0.4153	0.3885	0.5073	0.4350	0.4311
	0.4105	0.3843	0.5020	0.4304	0.4263

NOTE: … indicates no comparison.

tinguish them. Test sample 16 had the greatest similarity of all the inks with test sample 41. Test sample 13, whose two λ were above 0.9800, but the third slightly smaller than 0.9800 (for example 0.9745), was also reckoned as the same with 41. This phenomenon might be caused by bad spectral quality. Proceeding as above, the 14 ink samples in the first group could be classified into six subgroups, which were reference samples 46, 41, 11, 51, 8, and 2. It was worthy to note that all three λ of the reference sample 2 spectrum were smaller than the 0.9800 used for comparison with all reference spectra, so 2 should be another subgroup.

Moreover, by comparison with the reference spectra of 46, 41, 11, 51, and 8 reference samples in the first group, the λ values of test samples 39 and 96 inks in the second group were within the range of 0.7656 to 0.3843, which proved that these two samples did not belong to any subgroup in the first group.

The 94 kinds of ink samples in the second group with carbonyl (C=O) were classified into 29 subgroups by the same method (choose different λ for different species).

When the artificial intelligence of pattern recognition was used to depict and resolve FTIR spectrum, the most important step was to get enough spectra from the same sample; the more spectra, the better λ. Meanwhile, the set of the weighing value (W_j) was very important. The interference came from CO_2 between 2600 to 2000 cm^{-1} and mainly from H_2O in the air between 4000 to 3200 cm^{-1}, the $W = 0$ was set to 0 in these two ranges in order to exclude the interference. $W = 50$ was defined in order to making the key peak at 1265 to 1280 cm^{-1} more effective in pattern recognition. $W = 1$ was used for other spectral range.

The Inks Changing with Time

The KBr plate with ink strokes was put into temperature control accessory, setting the temperature at 50, 100, and 150°C and timing 1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 15, 18, 21, and 24 min for each. It can be seen that as the temperature and the time increased, the absorbance band at 1494, 1296, 1245, 1094, and 1055 cm^{-1} decreased, especially the peak at 1245 cm^{-1} which almost disappeared. This is due to the changes of the epoxy resin and the volatilization of solvents in the inks.

Figures 3 and 4 show the changes of the absorption bands at 1584 and 1360 cm^{-1} after heating test sample 46 at 100°C, from 1 to 24 min, respectively. The absorption band at 1584 cm^{-1} corresponding to the phenyl ring skeletal vibration weakened fast at the first 5 min and the peak height ratio slowed down. It must be emphasized that absorption bands at 1364 cm^{-1} overlapped the stretching vibration of C_{Ar}-N of tert-amine the triarylmethane dyes and the symmetrical stretch vibration of CH_3 in the epoxy resin. These two absorption bands at 1364 and 1360 cm^{-1} went down, but the absorption band at 1364 cm^{-1} decreased faster than the absorption band at 1360 cm^{-1}. It probably was that decomposition rate of triphenylmethane dye was faster than the cross-linking rate of the resin. When the cross-linking process on the surface of the ink finished, the triarylmethane dye inside paper decomposed more slowly. That is why the absorption band of the triarylmethane dye went down slowly.

The experimental results on UV irradiation were similar to the heating results, but exposure time changed from 1 to 12 h. The absorbance changed a little before and after exposure to ultraviolet light, but the frequency did not change. Using the Perkin-Elmer FTIR Spectrum software (V2.00), we calculated the corrected peak height of the inks (three times per sample). As a base line, 3700 and 2700 cm^{-1} were selected in the region of 4000 to 2000 cm^{-1}, and the 1790 and 880 cm^{-1} were selected in the region of 2000 to 400 cm^{-1}. Table 2 shows the result of the corrected peak height and their ratio of relation peak height for test sample 96.
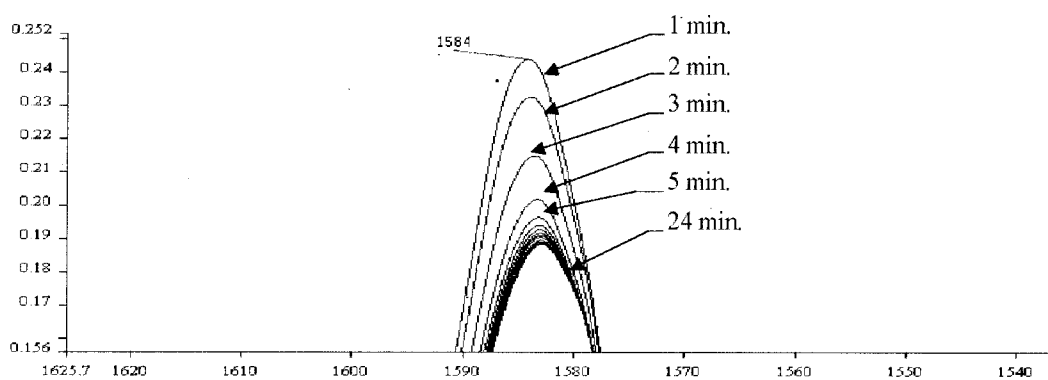
FIG. 3—*The changes of the absorption bands at 1584 cm^{-1} heating ink sample 46 at 100°C from 1 to 24 min, respectively.*
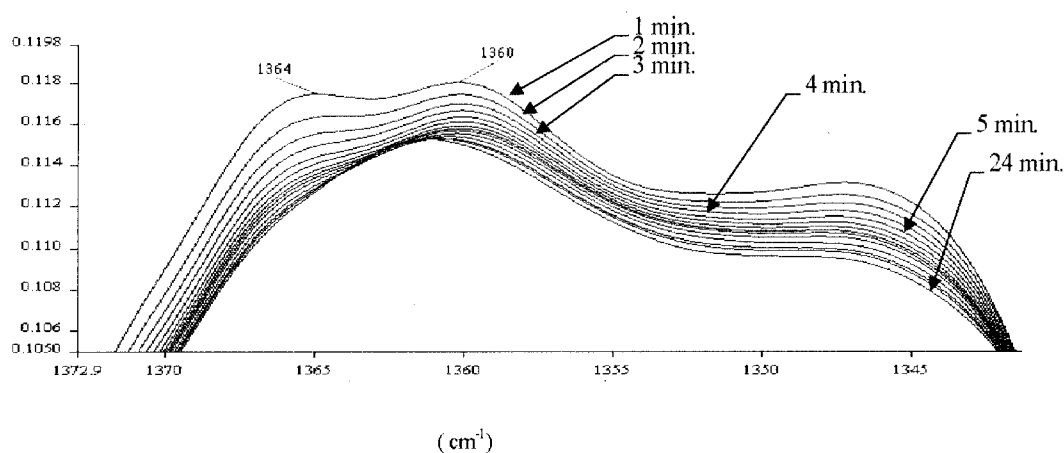

(cm^{-1})

FIG. 4—*The changes of the absorption bands at 1364 and 1360 cm^{-1} heating ink sample 46 at 100°C from 1 to 24 min, respectively.*

TABLE 2—*The corrected peak height and their ratio of the relation peak height for test sample 96 (aged with UV).*

| Time (hour)	Corrected Height				Ratio of Relation Height		Average Ratio of Relation Height	
	h_{1376}	h_{1285}	h_{1073}	h_{1041}	$H_{1285/1376}$	$H_{1041/1073}$	$Y_{1285/1376}$	$Y_{1041/1073}$
0	0.0582	0.1702	0.0866	0.0416	2.924	0.480	2.906	0.485
	0.0598	0.1728	0.0886	0.0434	2.890	0.490		
	0.0611	0.1775	0.0903	0.0437	2.905	0.484		
2	0.0407	0.1107	0.0598	0.0330	2.720	0.552	2.717	0.553
	0.0351	0.0953	0.0521	0.0287	2.715	0.551		
	0.0430	0.1168	0.0629	0.0350	2.716	0.556		
4	0.0372	0.0974	0.0544	0.0318	2.618	0.585	2.571	0.587
	0.0327	0.0825	0.0471	0.0280	2.523	0.594		
	0.0397	0.1021	0.0559	0.0325	2.572	0.581		
6	0.0244	0.0629	0.0344	0.0202	2.578	0.587	2.576	0.588
	0.0313	0.0809	0.0439	0.0257	2.585	0.585		
	0.0331	0.0849	0.0464	0.0275	2.565	0.593		
8	0.0360	0.0860	0.0484	0.0304	2.389	0.628	2.372	0.626
	0.0302	0.0711	0.0407	0.0250	2.354	0.614		
	0.0267	0.0576	0.0336	0.0214	2.157	0.637		
10	0.0387	0.0935	0.0524	0.0331	2.416	0.632	2.426	0.662
	0.0338	0.0822	0.0467	0.0287	2.432	0.615		
	0.0347	0.0843	0.0483	0.0299	2.429	0.619		
12	0.0359	0.0869	0.0498	0.0319	2.421	0.641	2.408	0.642
	0.0322	0.0767	0.0444	0.0290	2.382	0.653		
	0.0331	0.0801	0.0455	0.0288	2.420	0.633		
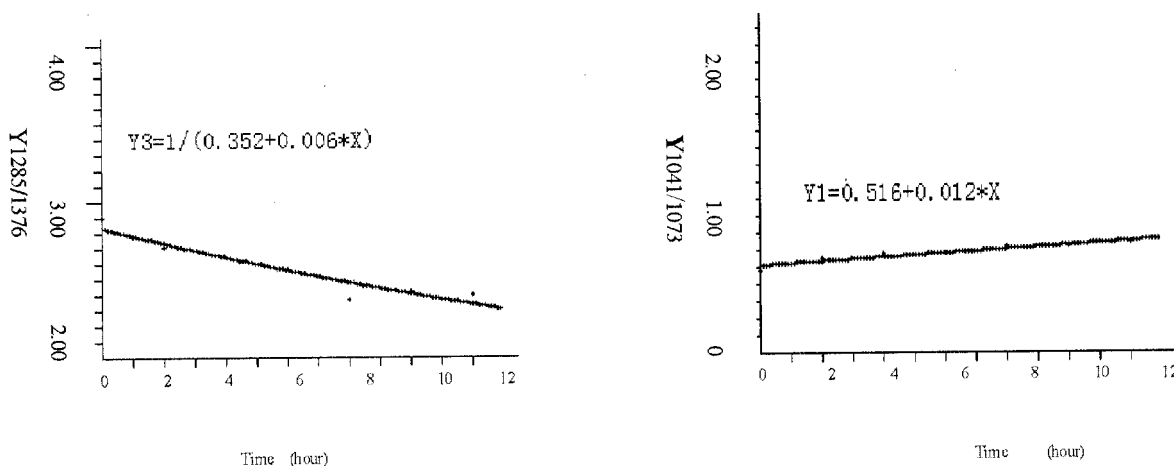
FIG. 5—(a) $Y'_{1285/1376}$ ratio of sample 96. The relationship between Y' of sample 96 and time ($Y' = $ peak height ratio) 1285 v. 1376 cm^{-1}. (b) $Y'_{1041/1073}$ ratio of sample 96. The relationship between Y' of sample 96 and time (1041 v. 1073 cm^{-1}).

After the calculation and calibration of peak height, the relative peak height ratios of the specific bands were used to express a change relation to time. According to the curve fitting, the relationship of test sample 96 was set up, i.e., $Y'_{1285/1376} = 1/(0.352 + 0.006 \times X)$ and $Y'_{1041/1073} = 0.516 + 0.012 \times X$. Figures 5a and b show two curves fitting ratio and time for test sample 96. Here, two relational expressions would be used for each ink in order to minimize their errors. The experiment results showed that the above changed rule depended on the formula of blue ballpoint pen inks. To express the blue ballpoint ink aging was also possible, and their changed rule depended on the components of the inks.

Conclusion

FTIR microscopy proved to be a useful tool in the analysis of the bulk blue ballpoint pen ink. By this method, not only were the components of the ink determined, but also the classification had been made. On the basis of this, the pattern recognition system of artificial intelligence was made to describe the frequency and absorbance of the spectra in detail. More importantly, the pattern recognition technology could identify the inks automatically and digitally. This was a new way to determine the bulk blue ballpoint pen inks; it is fast, accurate, and nondestructive.

It is well known that ink components could oxidize, cross-link, polymerize, and evaporate in the air. Through heating the ink strokes on a KBr salt plate or exposing it on UV light, the variation of some absorption bands at 1000 to 1600 cm^{-1} took place with time, and the relationship between peak height ratio and time was found. It means that some components in the inks would be changed. For example, the absorption bands of the resins decreased faster than the absorption bands of the dyes in ink. By using the linearity fitting, the equation between ink and the timing has been derived. In summary, this systematic analysis method for the blue ballpoint inks provided a basis for the examination of the identity and dating of ballpoint ink.

References

1. Merrill RA, Bartick EG. Analysis of ballpoint pen inks by diffuse reflectance infrared spectrometry. J Forensic Sci 1992;37:528–41.
2. Brunelle RL. Ink dating the state of the art. J Forensic Sci 1992;37:113–24.
3. Tebbett IR. The use of HPLC with multiwavelength detection for the differentiation of non ball pen inks. J Forensic Sci 1992;37:1149–57.
4. Cantu AA. On the relative aging of ink—the solvent extraction technique. J Forensic Sci 1987;32:1151–74.
5. Lyter AH. Examination of ball pen ink by high pressure liquid chromatogaphy. J Forensic Sci 1982;27:154–60.
6. Shoji KT. Discrimination of cinnabar seal inks affixed to paper-color test and fourier-transform infrared spectroscopy. Act Crim Japan 1990;56:19–29.
7. Xu X, De Koeijer JA, De Meel JM, Logtenberg H. Ink analysis for forensic science application by micellar electro kinetic capillary chromatography with photo-diode array detection. Int J Forensic Document Examiners 1997;3:240–60.
8. Stewart LF. Ballpoint ink age determination by volatile component comparison—a preliminary study. J Forensic Sci 1985;30:405–11.
9. Harrick NJ. Developments in IR-VIS-UV accessories from harrick scientific. An informational supplement to our catalogue HSC-831; Ossining, New York: Harrick Scientific Corporation, 1989;10.
10. Zeichner A, Levin N, Klein A, Novoselsky Y. Transmission and reflectance microspectrophotometry of inks. J Forensic Sci 1988;33:1171–84.
11. Harris JS, MacDougall D. Characterization and dating of correction fluids on questioned documents using FTIR. Can Soc J Forensic Sci 1989;22:349–76.
12. Humecki H. Experiments in ballpoint ink aging using infrared spectroscopy. Presented at the International Symposium on Questioned Documents held at the Forensic Science Research and Training Center, F.B.I. Academy, Quantico, VA, 1985.
13. Kazem K, Seyyed HA, Ahmadi G, Simultaneous RA. Determination of the pesticide naptalam and its metabolites in natural water by fourier transform infrared spectrometry. Analyst 1999;124:367–71.
14. Roger WJ, John FM. Transient infrared transmission spectroscopy. Anal Chem 1990;62:2247–51.
15. Pfefferli PN. Application of microspectrophotometry in document examination. Forensic Sci Int 1983;23:129–36.

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