Forensic Discrimination of Ballpoint Pen Inks Based on Correlation of Data Obtained by Optical and Spectral Methods

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*In routine examination of inks used on questioned documents a series of the nondestructive analytical methods, such as microscopic and optical techniques have been previously applied. However, they are often insufficient to identify the inks used for the preparation of the document. The aim of this work was to evaluate the possibility of discrimination among different inks provided from various sources by corroborating the data obtained by optical and spectrometric methods, such as UV-Vis-NIR, FT-IR and Raman spectroscopy, all of them being recognized as techniques used in forensic science. Surface Enhanced Resonance Raman Scattering technique (SERRS) does not destroy the sample, so that it remains as a valuable nondestructive spectroscopic analysis. Ultraviolet visible near-infrared spectrometer (UV-Vis-NIR) has been used to discriminate a series of ballpoint pen inks within the same coloristic pallet with some degree of success, particularly by a detail use of chromatic analysis provided by CIE L*a*b* analysis.*

Keywords: ink analysis, reflectance, FT-IR and Raman spectroscopy, chromatic analysis

Examination of suspect documents is one of the oldest branches of forensic science. The introduction of new writing materials together with increased literacy led naturally to an increase in the activities of the writing forger. Such forgery usually takes place in documents such as cheques, passports, birth certificate, etc.

Over the past 40 years, document examiners have strived on the scientific examination and identification of writing inks [1]. Most documents are made from paper and completed in ink that were written by writing instruments such as pencil, ball-point pen, fountain pen, gel pen or other substances which can be used for the same purpose [2]. Ink analysis is an important procedure that can reveal useful information about the questioned document.

Moreover, modern inks contain many substances aiming to improve ink characteristics [3]. Ballpoint pen ink usually contains a dye or several dyes in a viscous liquid, which is a mixture of natural or synthetic polymers and solvents. The ink contains also acidic compounds, which decrease its coefficient of friction during writing. Additionally, substances which inhibit drying of the paste and ensure its suitable viscosity are added. The detailed recipes are patented. Usually, in the literature, there is no complete information on the composition of ballpoint pen ink provided by various producers. It is only known that, apart from other components, they also contain some insoluble pigments [4].

The initial analysis of ballpoint pen inks is currently carried out using nondestructive methods such as visible, ultraviolet, and infrared light examination. However, nondestructive methods are useful only for answering the question of whether two or more documents could have the same origin. When more detailed information is required, some form of destructive chemical examination must be used [5]. Other non-destructive techniques include Raman [6] and surface-enhanced resonance Raman spectroscopy (SERRS) [7], UV–Vis spectrometers [8], although the spectrum quality for last method is heavily sample dependent [9].

In routine examinations of inks, some non-destructive analytical methods, such as microscopic and optical, are primarily applied [10, 11]. These methods allow chosen parameters of the ink to be characterized, such as its colors, luminescence and absorption of radiation. Samples may be differentiated on the basis of transmission, reflection and fluorescence spectra obtained for inks deposited on the surface of paper [12].

Fourier infrared spectroscopy (FTIR) has been also successfully applied in the analysis of inks. Advantage of the FTIR is that it is a non-destructive method. On the other hand, FTIR analysis requires minimal sample preparation and cost effectiveness [13]. Due to its non-destructive nature, Raman spectroscopy is also intensively applied in forensic investigations for the identification of inks directly on the document and for the determination of the sequence of the handwritten lines. This method is characterized by a better selectivity than other non-destructive techniques, such as luminescence in visible or in infrared light. Good signal-to-noise ratios as well as short time of measurements and low power laser are their main advantages [4, 14, 15].

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. However, these limitations can largely be overcome using the technique of SERRS. Raman signals are enhanced through resonance effects and by SERRS. 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 [16, 17]. The surface enhancement is achieved through use of colloidal gold aggregate. This technique involves applying

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over the sample at the point of analysis of a thin layer of gold colloid and poly L-lysine. This technique does not damage the sample, so that it is considered as one of the most important non-destructive spectroscopic analysis. Not only are the Raman signals further enhanced, but the presence of colloidal gold largely quenches the fluorescence [16, 17].

For ballpoint pen ink, in particular, UV/Vis/NIR reflectance spectrum is immensely informative. The reflectance spectra permit to distinguish writings made by different pen classes or by pens that work with different ink formulas. Therefore, studying the UV/VIS/NIR spectra it is possible to verify the presence of fraudulent manipulations. This technique is straightforward to execute and provides fairly rapid and repeatable results [18].

However, such optical and spectrometric methods do not provide information on all components of the ink and they do not allow identifying the kind of ink on the basis of its chemical composition. They take into account only those components, which strongly interact with a given region of electromagnetic radiation and therefore they show merely differences between compared samples [4].

Differentiation of inks through their infrared spectra is achieved based on the peaks position and their relative intensity, while in Raman spectroscopy the course and shape of the background curve - which depicts the fluorescence intensity of the examined material - is also relevant [11].

The aim of this paper is to evaluate the possibility of discriminating among a number of 18 ballpoint pens provided from various sources by corroborating the data obtained by optical and spectrometric methods, such as UV-Vis-NIR spectroscopy in diffuse reflectance mode, FT-IR spectroscopy, Raman spectroscopy and chromatic analyses in CIE-L*a*b*, all of them being recognized as non-destructive techniques in forensic science.

Experimental part

A number of 18 ballpoint pens were purchased from the market, to form a collection of ballpoint pens, available now in Romania, and having the following colors: 10 – blue, 3 – red, 3 – black and 2 – green. Trademark, manufacturer name and code of each of sample acquired are shown in table 1.

Table 1

INFORMATION ON BALLPOINT PENS USED IN THIS STUDY

Nr. Crt.	Trademark - Producer	CODE
	Blue ballpoint pens	
1	AIHAO - CHINA	A1
2	AIHAO- CHINA	A2
3	BIC - FRANCE	B1
4	BIC- FRANCE	B2
5	BIC- FRANCE	B3
6	BIC- FRANCE	B4
7	CORVINA51 - ITALY	C
8	LEGEND - ROMANIA	L
9	PELIKAN-GERMANIA	P.E.
10	PIANO30 - PAKISTAN	P.I.
	Red ballpoint pens	
1	BIC- FRANCE	B.R.
2	CORVINA 51- ITALY	C.R.
3	PELIKAN-GERMANY	P.R.
	Black ballpoint pens	
1	BIC- FRANCE	B.N.
2	PELIKAN-GERMANY	P.N.
3	PENTELSUPERB - EUROPE	PS.N.
	Ballpoint pens green	
1	CORVINA 51- ITALY	C.V
2	PIANO30- PAKISTAN	P.V

Optical examination

For optical analyses using nondestructive methods, each ballpoint pen was deposited on a sheet of paper in the form of points with a diameter of 3 mm, and a code has been assigned to each sample. All of the ballpoint pens were analyzed using different methods.

Determination of the optical properties of all ballpoint pens has been primarily performed by using reflected infrared radiation from the illumination by visible – infrared light spots between 530 and 1000 nm, and their brightness was observed by using a comparator video spectral - VSC 5000 Freeman Foster Company, UK. All the samples of the same color were observed while the examination was made in the same conditions to avoid any modification of light factors.

FT-IR analysis

To highlight the vibration behaviour of molecules existing in the composition of ballpoint pen inks, infrared spectra of all the samples have been submitted as a film on a KBr window, and then analyzed by transmission, using a FT-IR type Bruker Tensor 27 IR microscope coupled with a Hyperion 2000 type, provided by Bruker Optics, Germany. Infrared spectrum was recorded for each sample spectrum between 400cm^{-1} - 4000 cm^{-1}.

Raman spectroscopy

All samples have been studied under the action of laser light using Raman spectral comparator FORAM 685-2, provided by Foster-Freeman, England. This was done by placing each sample on paper under video microscope objective lens provided with rotating lens allowing magnification 10x, respectively, 20x and each deposit of ballpoint pen sample was examined by a “test window” of 5 mm. Laser radiation wavelength was 685 nm excited (spectral range 400-2000 cm^{-1}), acquisition was performed by mediation of 5 spectra.

Moreover, for the ballpoint pen samples that under laser irradiation shown a strong fluorescence, which makes difficult to observe Raman peaks, a thin layer of gold colloid and poly L-lysine has been applied over the sample. Thus, the SERRS technique has been used (Surface Enhanced Resonance Raman Scattering), which enhances the Raman spectrum while reducing the fluorescence.

UV-Vis/chromatic analysis

For the analysis by UV-Vis reflectance spectrometry, all the samples were deposited on a square sheet of paper of 2x2 cm size. These samples were analyzed using a Jasco 670 spectrometer in the UV-Vis domain, from 300-800nm, provided with a diffuse reflectance integrating sphere, a similar clean square sheet of paper being used as reference. The objective analysis of sample color has been performed by using the soft-ware on CIE L*a*b* system provided by Jasco.

Results and discussions

Optical examination

After the spots were examined under light between 530 and 1000 nm for all the ballpoint pen inks they were photographed and the analysis of their images resulted in the following conclusions.

For blue ballpoint pen inks, which are most numerous, only P.E., B4 and C samples could be discriminated from the other similar inks by both reflected infrared and luminescence photographs.

For red ballpoint pen inks, C.R. sample behaviour is different from that of samples B.R. and P.R.

For black ballpoint pen inks, the three samples can be distinguished by this method.

The two green ballpoint pen inks can not be distinguished by this method.

FT-IR spectroscopy

The IR spectra of inks showed a large peak at 3200 cm^{-1} to 3600 cm^{-1}, this indicating the presence of associated OH groups in the inks formulations [19]. Regarding the chemical composition of the tested pen inks, by viewing by FT-IR spectra (figs. 1-5) it can be presumed that almost all the 18 ballpoint pens present multiple functional groups (e.g. hydroxyl, carbonyl, amino, nitro, ester/ether groups). For instance, all the 18 ballpoint pens present the strong band of carbonyl (C=O) from 1720 – 1725 cm^{-1}, and an intense peak at about 1170 cm^{-1}, characteristic for the asymmetrical bending vibration of C-O-C bonds. This last band completed by the appearance of the symmetric vibrations of C-O-C from about 940 cm^{-1} (more evident for the B2 and B3 inks) confirms the presence of saturated ethers in ink composition. Beside this aliphatic ethers the strong band for all ink samples observed at 1245 cm^{-1} - 1294 cm^{-1} in the ink samples could also suggest the presence of aromatic ether (Ar -O) (e.g. A1 and A2 samples present intensive band at 1294 cm^{-1}). The strong band which appeared between 1580 – 1600 cm^{-1} represents a clear evidence of some amino groups (δ N-H). This last aspect is confirmed by the appearance of ν C-N from about 1050 – 1100 cm^{-1}. Another band that can be observed in almost all the samples is the peak from about 1380 cm^{-1} which can be assigned to the N-O groups. The spectra also exhibited peaks at the region of 2857 cm^{-1} to 2900 cm^{-1} indicating the CH_3 and CH_2 stretching bond vibrations.

Raman spectroscopy

The spectral results obtained for samples of blue ballpoint pens (fig.6), using Raman spectroscopy, have

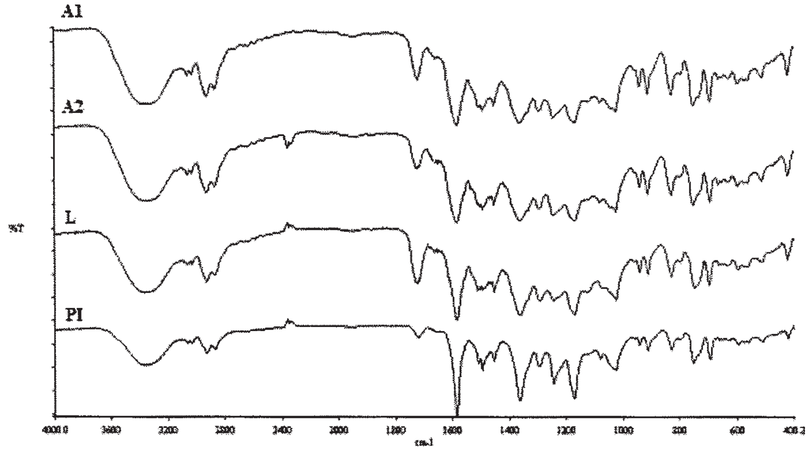

Fig. 1 IR spectra of blue ink ballpoint pens inks (samples A1, A2, L and P.I.)

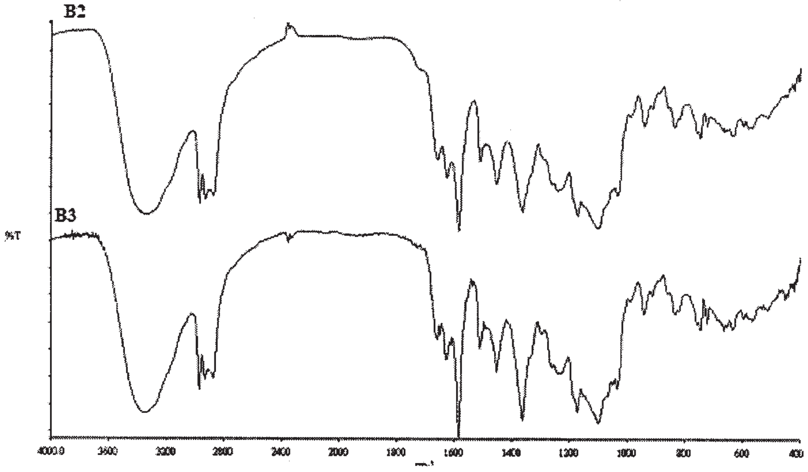

Fig. 2 IR spectra of blue ballpoint pens inks (samples B2 and B3)

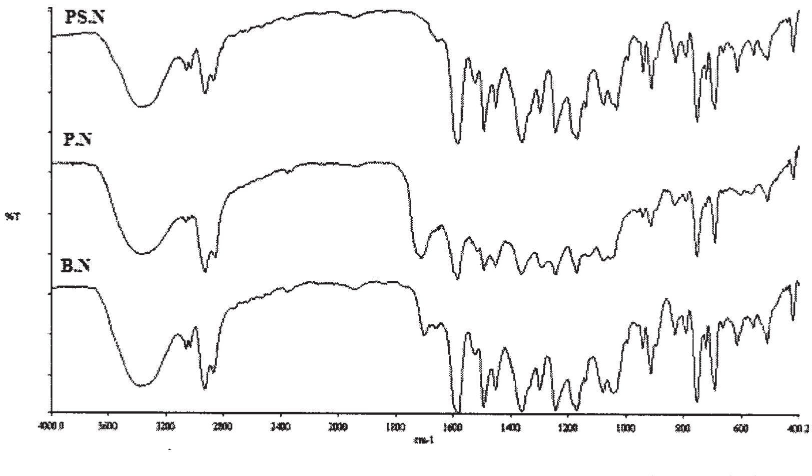

Fig. 3 IR spectra of black ballpoint pens inks

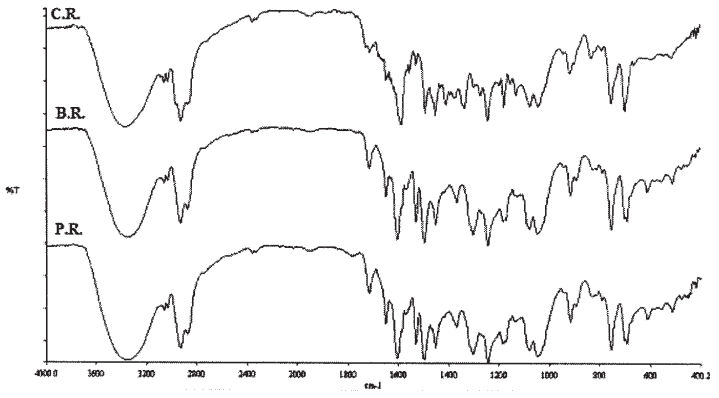

Fig. 4. IR spectra of red ballpoint pens inks

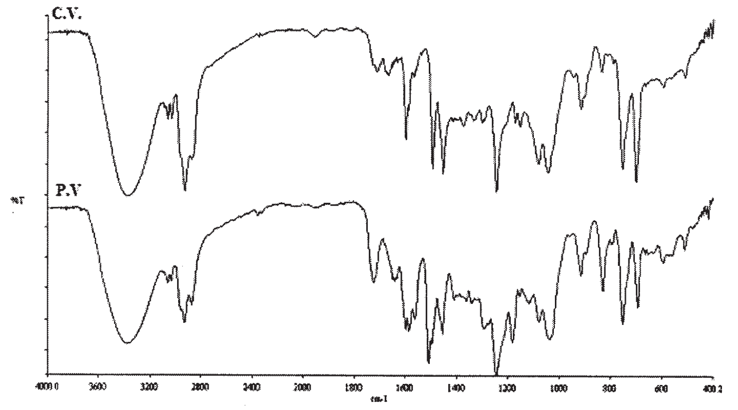

Fig. 5. IR spectra of green ballpoint pens inks

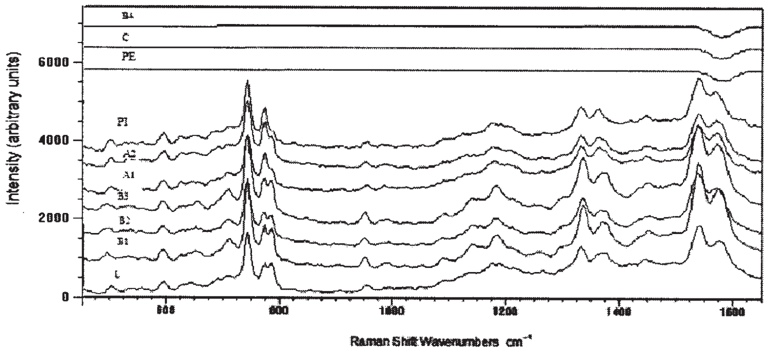

Fig. 6. Raman spectra of blue ballpoint pens inks

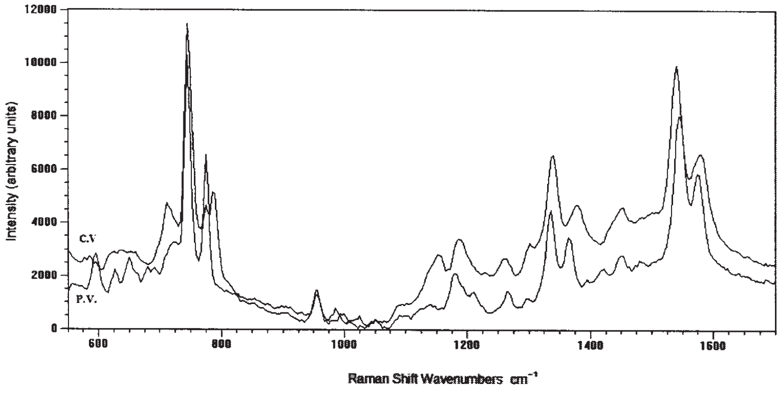

Fig. 7. Raman spectra of green ballpoint pens inks

shown that one can differentiate among these samples by using this method, as follows.

Samples B4, C and P.E. have spectral lines flattened by the presence of fluorescent components, leading to lower Raman signal, these samples being different as compared to the others samples.

Samples A1 and A2 have similar patterns, with the same peaks intensity.

Samples B1 and B3 show also similar patterns and peaks intensity, but they are different from the sample B2, since the peaks at 744 cm^{-1} in the region 1336-1372 cm^{-1} have a lower intensity, respectively in region 1541-1574 cm^{-1}. Sample L shows a similar conformation and the same peaks intensity in the region 726-802 cm^{-1} as the sample B2, and the same conformation and peaks intensity in the region 1156-1610 cm^{-1} with samples A1 and A2.

Sample P.I. is similar in the regions 714-776 cm^{-1} and 954-1610 cm^{-1} with samples A1 and A2, but without the peak at 788 cm^{-1}.

The spectral results obtained for samples of green ballpoint pen (fig. 7), using Raman spectroscopy, have shown that one can differentiate among the samples by using this method because the samples C.V. and P.V. present

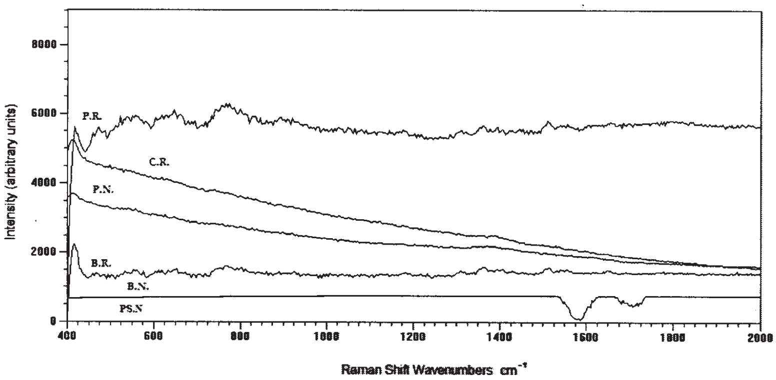

Fig. 8. Raman spectra of samples B.R., C.R., P.R., B.N., P.N. and PS.N.

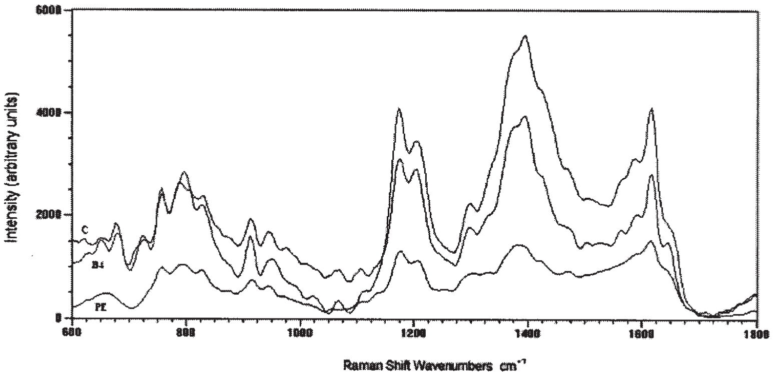

Fig. 9. spectra of samples B4, C and P.E.

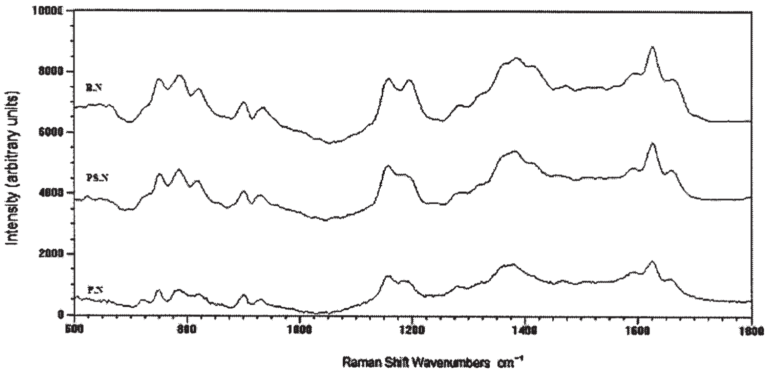

Fig. 10 . SERRS spectra of samples B.N., P.N. and PS.N.

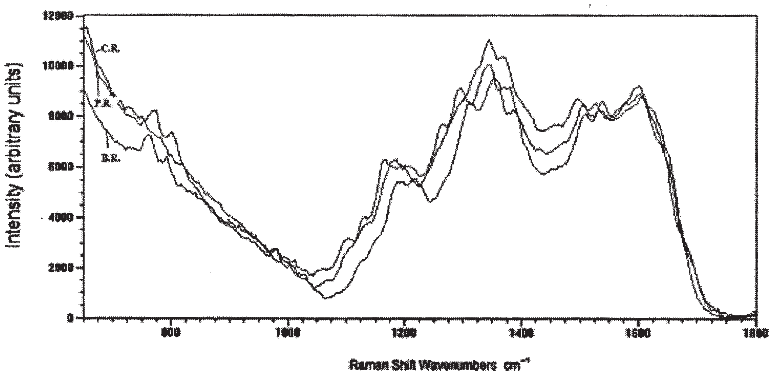

Fig. 11. SERRS spectra of samples B.R, C.R and P.R

both patterns and intensity of peaks located at different wavelengths.

Spectral results obtained for samples of black and red pen pastes are presented in figure 8. Spectral lines obtained from the analysis indicate the existence of some fluorescent components in the composition, which lead to lower Raman signal.

For these samples showing strong fluorescence emission the SERRS technique has been used. Spectral results are shown in figure 9 for the blue ballpoint pens samples, in figure 10 for the black ballpoint pens samples, and in figure 11 for the red ballpoint pens.

The analysis of these spectral results obtained by using SERRS technique shows the following aspects.

Samples B4 and C have the same pattern but a lower peak intensity on the entire spectral range for the sample C.

On the other band these samples (B4 and C) have much higher peaks intensity than the sample P.E. and distinct peaks at 725 cm^{-1}, 1067 cm^{-1}, 1298 cm^{-1} and 1588 cm^{-1}.

Moreover, the samples B4 and C show conformation and peak intensities from the other samples: A1, A2, B1, B2, B3, L and P.I.

Samples B.N., P.N. and PS.N are also different; indeed, in some regions they have different patterns and peak intensities: sample P.N. shows a distinct peak at 720 cm^{-1}, while B.N. sample shows distinct peaks at 1159 and 1199 cm^{-1}.

Table 2
TRICHROMATIC PARAMETERS OF BLUE BALLPOINT PENS

Sample	L*	a*	b*	C*	h*
A1	34.61	20.50	-20.90	29.28	314.45
A2	37.54	25.67	-29.81	39.34	310.73
B1	36.38	25.24	-42.71	49.61	300.59
B2	33.11	16.86	-24.04	27.26	298.16
B3	35.43	8.99	-20.26	22.17	293.92
B4	32.63	24.59	-32.55	40.79	307.06
C	33.15	26.53	-34.81	43.77	307.31
L1	36.14	23.14	-24.26	33.53	313.65
P.E.	37.24	36.77	-52.30	63.93	305.11
P.I.	34.54	19.89	-21.03	28.95	313.39

In a similar manner, the samples B.R., C.R., and P.R. are different as their conformation and intensity of peaks are located at different wavelengths.

UV-Vis analysis

CIE L*a*b* based analysis of the investigated samples can provide valuable tools in discrimination of different inks within the same coloristic pallet by means of all five parameters provided by the soft-ware, with the following significance [20]:

L* - represents the luminosity of the color (***L**** = 0 yields black and ***L**** = 100 indicates diffuse white; specular white may be higher)

a* - position between red and green axis (negative values indicate green, while positive values indicate red colors)

b*- its position between yellow and blue axis (negative values indicate blue and positive values indicate yellow colors).

C* - chrome (distance from the luminosity axis being an indication on homogeneity or complexity of the chromophore composition)

h* - hue angle, reflecting the proportion of colors provided by a* and b* parameters.

The trichromatic analysis of the samples investigated will be discussed in detail based on parameters collected in the tables 2-5. For instance, from the table 2, one can observe that for all the ten blue ink samples no one has any identical parameter when compare to each other. A more detail analysis reveals the following discriminative aspects.

The values of luminosity, L*, are ranging for all the samples between 32.63 (sample B4) and 37.54 (A2), which allow to arrange the inks on an intensity scale, from light blue to dark (more intense) blue.

As referring to planar chromatic parameters, one can notice that all a* values are positive, bringing the red contribution to the colors, while all b* values are negative, according to their blue colors. Once again one can order all blue samples against these values, noting the smallest value of a* around 8 (for B3 samples), and the highest b* value over 52 for b* parameter (P.E. sample).

However, a relevant contribution of these red and blue monochromatic colors to the final colors of the sample is provided by the hue angle, h*, which has already weighted their proportions into a unique parameter. Indeed, one now can order the samples of various tunes between indigo and violet, while the hue angle is changed from 293 (B3) towards 314 degrees (A1).

Such changes in colors tent are caused by various factors, the most important among them being chemical nature of the chromophore agent(s), their concentration, and the influence of the other ingredients of the ink. That is why, even though the complete composition of these inks could be difficult to be known or detected, the use of these chromatic parameters can provide information to identify an unknown ink among those registered in such a data base.

Moreover, the chroma, C* parameter, is also useful in such identification, as it provides an image on the "purity" of chromophores, more precisely if there are one or many pigments constituents of the ink. For instance, the C* value is relatively high, as in case of P.E. sample (over 63), suggesting the presence of one dye, while the smallest value of chroma for B3 sample (22.17) is the result of a more complex pigment composition. Once again one can notice that these two extreme samples are also discriminated by means of other nondestructive techniques, while chromatic analysis can also detect much smaller differences among various inks belonging to the same colorist class.

A similar analysis made on inks of different colors, even though performed on a smaller number of samples, is highly relevant for discrimination among similar samples. Indeed, the three red inks (table 3) exhibit significant different values for all chromatic parameters, with positive values for both a* and b*, and preponderance of a*, in accordance with their main red colour.

Table 3
TRICHROMATIC PARAMETERS OF RED BALLPOINT PENS

Sample	L*	a*	b*	C*	h*
C.R.	43,49	44,23	20,30	48,67	24,65
P.R.	50,63	52,98	29,97	60,87	29,50
B.R.	47,26	46,08	24,60	52,24	28,09

For green inks (table 4) are specific the negative values for a* parameter, while the difference between the two samples is also evidenced by the big difference of chroma, this illustrating the major differences in composition and number of pigment agents.

Analysis of black inks (table 5) seems to be rather complicated and maybe less relevant to be used for sample

Table 4
TRICHROMATIC PARAMETERS OF GREEN BALLPOINT PENS

Proba	L*	a*	b*	C*	h*
P.V.	34,23	-6,99	0,66	7,02	174,57
C.V	50,20	-36,84	3,02	36,97	175,32

Table 5
TRICHROMATIC PARAMETERS OF BLACK BALLPOINT PENS

Proba	L*	a*	b*	C*	h*
B.N.	33,04	8,75	1,88	8,95	12,10
P.N	31,58	6,66	-1,65	6,86	346,05
PS.N	33,13	7,91	4,63	9,17	30,33

discrimination, since all chromatic parameters show relative small and similar values and as a result, the differences observed might be not significative enough to distinguish among various sources. Thus, while a* is ranging between 6 and 8, b*and h* values might be either positive or negative. The value for chroma bellow 10 is also an indication for the complexity of chromophore mixture.

One can conclude that, except for black ink samples, the use of all 5 chromatic parameters can be assessed as a valuable tool in successful discrimination among similar ink colors. This affirmation is also supported by the possibility to register directly the deviations, L, for all these parameters, between the questioned ink and a known ink existent within data base of the operator.

Conclusions

The methods used in this study such as reflected infrared, infrared luminescence, FT-IR spectroscopy, Raman spectroscopy, UV-Vis spectrometry and chromatic analyses in CIE-L*a*b* are efficient methods in document analyses, since these methods do not alter the documents. They are especially useful when should be investigated financial documents, historical, passports, birth certificates, etc.

Surface Enhanced Resonance Raman Scattering technique does not damage the sample, so it can be also considered as a valuable non-destructive spectroscopic technique. It has been shown that SERRS spectroscopy dramatically enhances the usefulness of Raman based techniques. Samples which are either inherently IR fluorescent 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.

Trichromatic analysis based on processing CIE L*a*b* parameters exhibits a higher potential, not enough exploited till now, in discriminating the samples belonging to the same coloristic pallet, as it was demonstrated on different ball point pen inks investigated by a series of non-destructive optical and spectral techniques.

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