

Comparative Forensic Analysis of Ballpoint Pen Inks

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*Forensic examination of questioned documents often includes identification, separation and determination of the components of ink that are deposited on the paper during the writing process. There are many possibilities leading to the development of methods for ink analysis. This paper aims to assess the possibility of discriminating in a forensic analysis of a series of ballpoint pastes and identify the dyes used for ballpoint pen inks using X-ray fluorescence, thin layer chromatography (TLC) and UV-Vis-NIR spectroscopy in diffuse reflectance and absorbance modes completed by chromatic analysis in CIE-L*a*b* system. Corroboration of trichromatic analysis, particularly that performed in methanolic extracts, with TLC data provides a valuable tool for discriminating of ballpoint inks within the same coloristic pallet and also for assessing some components by comparing with reference dyes available from adequate data bases.*

Keywords: ballpoint inks, dyes, thin layer chromatography, chromatic analysis

Forensic examination of questioned documents often includes identification, separation and determination of the components of ink that are deposited onto paper during the writing process [1].

Document is a unavoidable evidence in forensic caseworks because it is correlated to human daily life. Most of them are made from paper and completed in ink when this was 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].

When documents are examined for forensic purposes, discrimination of inks and/or identification of their source are an important issue [3]. The forensic examination of inks is principally concerned with the classification and comparison of chemically complex mixtures of dyes, pigments and other materials, usually present in handwriting on a document [4].

Dyes are soluble in the liquid body of the ink, which is also known as the vehicle [3, 5, 6]. On the other hand, pigments are finely ground multi-molecular granules that are insoluble in the vehicle. The vehicle, whose composition affects the flowing and drying characteristics of the ink, can consist of oils, solvents and resins. Other substances used for finely tuning the characteristics include driers, plasticizers, waxes, greases, soaps and detergents [7, 8].

The analysis of inks is reduced to the analysis of dried inks; their complex composition remains a challenge to the forensic scientists. Among available analytical techniques, physical and chemical methods can be distinguished. Physical methods are preferred for the investigation of documents since they are nondestructive to the evidence in most cases. Comparisons of inks with genuine samples which may aid in the identification of the questioned materials can be achieved using optical microscopy, microspectrophotometry and various modes of IR and UV/Vis spectroscopy [9]. When more detailed information is required, some forms of destructive chemical examination must be used [3].

Ultraviolet-visible-near infrared spectrophotometry (UV-Vis-NIR) and Fourier Transform Infrared Spectrometry (FTIR) can be also used to pen brand differentiation. Identification of an ink formulation may be important for questioned document examination. Knowledge of ink formulae can help to determine the authenticity of a document, including age and presence of any changes to the document [7, 10].

Chromatographic techniques which involve the removal of a small amount of ink from a document and the separation and subsequent comparison of the chromatogram to those of standards are very useful. Thin layer chromatography (TLC) is the primary analytical technique used for the analysis of inks in the forensic laboratory [11-13].

The solvent used in ballpoint pen ink volatilizes gradually. However, the non-volatile nature of the dyes in these inks makes the dyes very valuable to the forensic scientist because the dyes remain on paper in the form of letters, marks or lines after the solvent has been evaporated [14, 15].

This paper aims to assess the possibility of discriminating in a forensic analysis of a series of ballpoint pastes and identifying the dyes used for ballpoint pen inks using X-ray fluorescence, thin layer chromatography and UV-Vis-NIR spectroscopy in diffuse reflectance and absorbance modes completed by chromatic analyses in CIE-L*a*b* system.

Experimental part

A number of six ballpoint pen inks (red and black) have been purchased, to form a collection, available now in Romania, with their specifications shown in table 1. A reference data basis of color dyes used for ballpoint pen inks has been examined and their identification names are presented in table 2.

UV-Vis spectrometry and chromatic analysis

UV-Vis spectrometry and chromatic analysis of the samples have been performed in two distinct ways: in reflection mode for the inks and dyes such as, and in absorption for their methanolic extracts.

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Table 1
INFORMATION ON BALLPOINT PENS USED IN THIS STUDY

Nr. Crt.	Trademark - Producer	CODE
Red ballpoint pens		
1	BIC- FRANCE	B.R.
2	CORVINA 51- ITALY	C.R.
3	PELIKAN-GERMANY	P.R.
Black ballpoint pens		
4	BIC- FRANCE	B.N.
5	PELIKAN-GERMANY	P.N.
6	PENTELSUPERB - France	PS.N.

Table 2
SUMMARY OF IDENTITY SPECIFICATIONS FOR THE
REFERENCE DYES (RED, YELLOW AND BLUE)

Nr.	Chemical name	Common names	Cod
RED DYES			
1	Pigment red 52:1	Rubin Litoner	PR52/1
2	Pigment red 81	Fanal Rosa	PR81
3	Pigment red 4	Permanent Red R	PR4
YELLOW DYES			
4	Lead chromate	Chrome Yellow	GC
5	Acid yellow 23	Tartrazine	AY23
BLUE DYES			
6	Acid blue 3	Patent Blue V	AB3
7	Acid blue 13	Acilan Violet 10B	AB13
8	Basic violet 3	Crystal Violet	BV3
9	Acid blue 83	Brilliant Blue	AB83

The samples of ballpoint inks and the reference colour dyes were mixed with magnesium oxide powder and analyzed in the tablet form. These samples were analyzed using a Jasco 670 spectrometer in the UV-Vis domain, between 300-800nm, provided with a diffuse reflectance integrating sphere, using as reference the white standard of spectrometer.

In the second case, each sample was deposited on a fragment of white paper, forming a square of 1 cm side, then inserted into a 5 mL glass tube and extracted with methanol. For complete extraction of ink components from paper matrices they were vigorously shaken for 1min. Colouring components were dissolved in methanol. Also, small amounts of reference dyes were subject to methanolic extraction and analyzed using the same instrument but now in absorbance mode, with methanol used as the reference solvent.

The objective analysis of sample color has been performed by using the software on CIE L*a*b*system provided by Jasco.

Thin-layer chromatography - TLC

In order to determine the optimal solvent extraction various solubilizing trials of ballpoint inks (black and red) have been checked, and the solvents used and the solubility of the pen pastes are shown in table 3.

Table 3
LIST OF SOLVENTS USED FOR THE EXTRACTION OF INK
COMPONENTS FROM PAPER

Nr. Crt.	Solvent	Solubility of ink colors
1.	Ethanol	slightly
2.	Butanol	slightly
3.	Ethyl acetate	slightly
4.	Cyclohexan	slightly
5.	Methanol	soluble

Following the solubility tests, methanol was chosen as the extraction solvent. As a result, for analysis by thin layer chromatography the methanol extract used in UV-Vis spectrophotometry was chosen, both for ballpoint inks and also for reference dyes. TLC analyses were performed using Kieselgel 60 plates made by Merck Art. 5721, without a fluorescence indicator. Methanolic extracts were spotted on TLC plates using micro capillary pipettes at about 1.5 cm from one end of the plate. Each ink group was spotted on a separate TLC plate and the spots were placed at a distance of 1 cm from each other. The diameter spots was of 3mm.

In order to develop a proper separation of colored elements, two systems were used:

- ethyl acetate / ethanol / water (7:3,5:3, v/v/v);
- *n*-butanol / ethanol/ water (3:3:1, v/v/v)

The chromatographic plates containing the methanolic extracts of the samples were placed in the developing tank, which contains both the solvent A system and the solvent B system. The tanks were hermetically closed for 30 min. After development, the plates were air-dried and separated compounds were visualized on the layer by their natural colour. Then the plates were scanned with ordinary office scanner. Values the retention factor, R_f , of the samples and pictures of each separate colour spots on a sample plate were measured and recorded.

X-ray fluorescence spectroscopy

Elemental composition of both reference dyes and ballpoint inks was analyzed using X-ray fluorescence spectrometry. Measurements were made with an X-ray type spectrofluorimeter EAGLE III, μ Probe, in vacuum, in the following conditions: excitation source - X-ray generator (Rh); voltage - 40 kV, current - 200 μ A; detector - Si(Li) monocalipar with 300 μ m spot; time constant of 17 μ s.

Both dyes and ballpoint inks samples were calcined to dry ash in the crucible at 500°C for 1 h. Four X-ray fluorescence measurements were made for each ink sample and the average composition was taken for each element.

Results and discussions

UV-Vis spectrometry and chromatic analysis

CIE L*a*b* based analysis of the investigated samples can provide valuable tool in discrimination of different inks within the same colouristic pallet by means of all five parameters provided by the software, with the following significance [16-19]:

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^* - position between yellow and blue axis (negative values indicate blue and positive values indicate yellow colors);

C^* - chroma (distance from the luminosity axis) is an indication on homogeneity or complexity of the chromophore composition;

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

These chromatic parameters registered in solid powders mixed with MgO and in methanolic extracts are collected for red samples in tables 4 and 5, and for black samples in the tables 6 and 7, respectively.

Trichromatic parameters	L*	a*	b*	C*	h*	color
Red ballpoint pens						
B.R.	84.78	18.44	-2.43	18.60	352.50	Pal pink
C.R.	85.89	12.09	-1.84	12.23	351.33	Pal purple
P.R.	90.25	13.82	-3.14	14.17	347.18	Pal pink
Red dyes						
PR52/1	73.85	25.41	-4.91	25.88	349.06	Purple
PR81	73.31	39.37	-13.41	41.59	341.19	Pink
PR4	63.64	22.39	12.72	25.75	29.60	Yellow brown

Trichromatic parameters	L*	a*	b*	C*	h*	color
Red ballpoint pens						
B.R.	89.76	25.83	-9.97	27.69	338.89	Pal pink
C.R.	88.39	34.60	-5.26	35.00	351.35	Pal purple
P.R.	93.60	18.93	-4.93	19.56	345.41	Pal pink
Red dyes						
PR52/1	87.41	28.77	9.36	30.26	18.01	Pal yellow purple
PR81	89.80	33.60	-10.19	35.11	343.12	Pal pink
PR4	86.05	3.96	27.89	28.17	81.91	Pal pink brown

For all the samples the luminosity parameter will not be discussed, being not relevant for this analysis in discriminating among various chromophore components. However, the other four parameters will be analysed in detail as follows.

For solid red samples (table 4) the dominant chromatic parameter is $a^* > 0$ as expected for red color, while b^* values are rather small, and usually negative as a reduced contribution of blue nuance both for ballpoint inks and reference dyes, except for the dye PR4 for which brings about a significant yellow contribution. Therefore, this last aspect excludes this reference dye as a possible component of the ballpoint inks analysed here.

The simultaneous contribution of a^* and b^* parameters is revealed by h^* values, which are located near and below the positive abscissa, except for the PR4 dye which is located on the first quadrant limited by red and yellow colours as discussed above.

The chroma, C^* , is also relevant, having smaller values for ballpoint inks than for reference dyes, in agreement with a higher complexity of the composition of the former as compared to the later samples.

Chromatic analysis of these samples in solution (table 5) generally shows a similar behaviour, except for the dye PR52/1 which contains a yellow colorant soluble in methanol ($b^* > 0$), which excludes once again this reference material as possible component within the red ballpoint inks analyzed.

For the black ballpoint inks (table 6) the smallest values for chroma, C^* , are obtained as compared with blue

reference dyes, both of them having smaller values when compare with red samples, thus revealing the highest heterogeneity of the chromophore mixture.

The dominant chromatic parameter corresponds now to blue tones ($b^* < 0$), as expected, that is why the blue reference dyes have been selected to identify some possible components of ballpoint inks taken for this study. In this respect the AB3 and AB83 dyes might be excluded from this assessment having $a^* < 0$ corresponding to green colour. This remark is supported by the chromatic analysis of these samples in methanolic extract (table 7) where contribution of soluble green colorant is much enhanced.

These preliminary assessments should be also confirmed by thin layer chromatography and X-ray fluorescence measurements.

Thin-layer chromatography - TLC

The chromatographic separation of ink into its constituent component dyes has proved to be a good method, not only for the comparison of the inks but also for matching ink to a database which contains the reference dyes.

From the study of chromatographic plates is observed that some of compounds separated from ballpoint inks exhibit similar shades of colour and the same R_f as the separated compounds of some reference colorants.

Thus, for a better identification of the methanol extracts, the ballpoint inks (black and red) were spotted on the same chromatography plate with methanol extracts of the selected reference colours having similar components

Table 4
TRICHROMATIC PARAMETERS OF RED BALLPOINT PENS AND REFERENCE DYES ANALYZED IN MgO

Table 5
TRICHROMATIC PARAMETERS OF RED BALLPOINT PENS AND REFERENCE DYES ANALYZED IN METHANOLIC EXTRACTS

Trichromatic parameters	L*	a*	b*	C*	h*	color
Black ballpoint pens						
B.N.	69.02	1.79	-11.24	11.38	279.03	Blue gray
P.N.	68.66	1.33	-9.61	9.71	277.87	Blue gray
PS.N.	68.14	0.91	-9.62	9.66	275.41	Blue gray
Blue dyes						
AB3	68.79	-6.48	-15.26	16.58	246.98	Greenish blue
AB13	70.01	6.86	-20.10	21.23	288.84	Purple gray
BV3	69.81	9.81	-20.11	22.38	295.99	Purple gray
AB83	78.71	-2.99	-8.24	8.77	250.66	Greenish blue

Table 6
TRICHROMATIC PARAMETERS OF BLACK BALLPOINT PENS AND REFERENCE BLUE DYES ANALYZED IN MgO

Trichromatic parameters	L*	a*	b*	C*	h*	color
Black ballpoint pens						
B.N.	72.45	20.46	-28.11	34.76	306.05	Purple
P.N.	78.79	22.56	-26.20	34.58	310.73	Pal purple
PS.N.	70.20	23.19	-30.34	38.19	307.39	Purple
Blue dyes						
AB3	91.34	-23.45	-14.27	27.45	211.32	Turquoise
AB13	75.82	24.28	-38.38	45.41	302.32	Purple
BV3	80.93	19.77	-31.33	37.04	302.25	Pal purple
AB83	89.97	-25.82	-16.49	30.64	212.57	Turquoise

Dye name	Color compound	R _f	Ballpoint pen
Crystal violet - BV3	Purple	0,34	P.N.
	Purple	0,48	
	Pal purple	0,53	
Acilan Violet 10B - AB13	Purple	0,34	B.N. PS.N.
	Purple	0,51	
	Purple	0,57	
Fanal Rosa - PR81	Orange	0,61	B.R. P.R.

Element	S	Cl	Ca	Fe	Na	Cr	Pb	Zn	Cu	P	Si
Sample Dyes											
AB3	56.7	5.6	-	-	37.3	0.4	-	-	-	-	-
AB13	83.3	-	9.2	7.5	-	-	-	-	-	-	-
BV3	9.4	86.7	-	3.9	-	-	-	-	-	-	-
AB83	100	-	-	-	-	-	-	-	-	-	-
GC	-	-	-	-	-	8.8	91.2	-	-	-	-
AY23	19.3	47	-	-	33.7	-	-	-	-	-	-
Black ballpoint											
B.N.	89.5	-	-	-	-	-	-	-	-	10.5	-
P.N.	3.6	63.7	-	4.6	-	-	-	6.7	10.5	-	10.9
PS.N.	93.1	-	-	-	-	-	-	-	-	6.9	-

Table 7
TRICHROMATIC PARAMETERS OF BLACK BALLPOINT PENS AND REFERENCE BLUE DYES ANALYZED IN IN METHANOLIC EXTRACT

Table 8
TLC RESULTS OF REFERENCE DYES AND BALLPOINT PENS

Table 9
ELEMENTAL ANALYSES OF REFERENCE DYES (BLUE AND YELLOW) AND BLACK BALLPOINT, CALCINED AS DRY ASH, %

separated and then eluted in the same system, namely A or B.

The colour tones of the compounds separated by TLC analysis of the methanolic extracts of ballpoint inks (black and red) and the afferent reference dyes, using the solvent system A, are shown in tables 8.

By comparing the retention factors, R_f , we arrived to the following conclusions:

- methanolic extracts of the sample noted B.R. and P.R. contain a compound separated of the same hue (orange) and retention factor R_f as for those obtained for PR81- Fanal rosa;

- methanolic extracts of samples noted B.N. and PS.N. exhibit some compounds separated of similar hue (purple) and retention factors R_f to the compounds separated from the reference dye noted AB13 - Acilan violet 10B;

- for the methanolic extracts of sample noted P.N. the compounds separated are of similar hue (pale purple and purple) and retention factor R_f as those obtained for BV3 - Crystal violet.

One can notice that these results are in perfect agreement with prevision preliminary assessment of the reference dyes in the ballpoint ink composition made by trichromatic analyses.

Similar TLC results have been obtained by using solvent system B, for ballpoint inks (black and red) and reference dyes, used in this study.

X-ray fluorescence spectroscopy

Determination of the elemental composition is very useful in the characterisation of ballpoint inks and the identification of reference dyes. Elemental composition of black ballpoint inks and standard dyes calcined is shown in table 9.

The analysis of data revealed the following aspects:

- the elemental analysis highlighted the presence of sulphur, chlorine and iron in the black ballpoint ink P.N., these elements being also present in the reference dye crystal violet (BV3), in accordance with chromatic and chromatographic analyses;

- the blue reference dye AB13 exhibits a high percentage of sulphur (83,3%); this element is found in black ballpoint inks B.N. and PS.N. in similar percentage, once again in accordance with previous data.

For red inks this technique provided no relevant data, probably due to the presence of other insoluble ingredients of different origins existent not necessary with chromophore purpose.

Conclusions

Trichromatic analysis of pen inks and reference dyes as powders in MgO provided a preliminary image on the complexity of real mixtures (by means of chroma parameter) and possible reference dyes to be present into the ink composition.

More accurate information is obtained by trichromatic analysis in methanolic extracts, where some reference

dyes are excluded from the ink composition, while some others are possible components of them.

TLC analyses bring about elements to support trichromatic analysis in solution, by confirming the presence of components with similar shades and R_f .

X-ray analysis X gives more relevant information for black than for red pigments, due to the possible interference of other ingredients.

One can conclude that corroboration of trichromatic analysis, particularly in methanolic extracts, with TLC data provided a valuable tool for discriminating of ballpoint inks within the same coloristic pallet and also for assessing some components by comparing with reference dyes available from adequate data bases.

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