ACTA·GRAPHICA
ISSN: 0353-4707
e-ISSN: 1848-3828
ZNANSTVENI ČASOPIS ZA TISKARSTVO I GRAFIČKE KOMUNIKACIJE
JOURNAL FOR PRINTING SCIENCE AND GRAPHIC COMMUNICATIONS

Scientific article

Characterization of Ballpoint Pen Inks

Marinović Veronika[1], Brzica Stjepan[1], Ledić Andrea[1]

[1]*Centar za forenzička ispitivanja, istraživanja i vještačenja „Ivan Vučetić", MUP RH*
vmarinovic@mup.hr

Abstract:

Analyzing ballpoint inks has always been a challenge for forensic scientists, since ballpoint pens can be used to create various types of forgeries. Ballpoint pen inks are mixtures that mainly consist of dyes, organic solvents and additives. More specific information about the composition of ballpoint pen ink is not available from the manufacturer due to confidentiality, and it is unknown, which dyes and other components are used by individual ballpoint pen ink manufacturers, so it is important to determine and identify the components of the ink. The basic approach in determining the differences in the composition of ballpoint pen inks is the identification of the dyes that make up the inks. Blue ballpoint pen inks usually contain triarylmethane dyes: Crystal Violet (CV), Methyl Violet (MV), tetramethylpararosaniline, (Tetra-PRS) and Victoria Blue B (VB). The chemical composition of the ink can be determined by different methods of chemical analysis, and in this work, the High Performance Liquid Chromatography (HPLC) method was used for the analysis of the ink. The characterization of the analyzed blue ballpoint pen ink samples was carried out based on the chemical analysis of the ink, i.e. by determining the chemical composition of the dyes and determining the similarities and differences in the qualitative and quantitative chemical composition of the detected components in the blue ballpoint inks of different manufacturers.

Keywords:
Characterization, Ballpoint pen inks, Dyes, HPLC, Forensics

1. Introduction

The role of chemical analysis in the examination of writing inks, and consequently of documents, has always been important in forensics, because chemical analysis can determine similarities and differences between ballpoint pens of different manufacturers. The basic approach in determining the differences in the ink composition is the identification of the dyes that make up the inks [1, 2]. It is very difficult to determine whether a particular pen was used to write a document, however, it is possible to identify the brand of a ballpoint pen, and in order to do this, it is necessary to classify different brands of ink [1]. Ballpoint pen inks are a mixture of dyes, organic solvents, resins and additives [1-4]. Dyes in inks can be divided into four groups: arylmethane, azo, phthalocyanine and azine [1, 2]. Triarylmethane (triphenylmethane) dyes are most often used: Crystal Violet (CV), Methyl Violet (MV) and Victoria Blue B (VB). The initial composition of the ink varies significantly depending on the shade of the ballpoint pen ink, but also varies between different brands of ballpoint pens [4]. Due to confidentiality, manufacturers do not provide specific information on the composition of the ink of ballpoint pens as well as on the processes of their decomposition, therefore it is important to determine and identify the components of the ink [2, 5, 6, 7]. In order to solve the lack of information about inks in different brands of ballpoint pens, it is necessary to carry out a chemical analysis and determine the quantitative composition, i.e. evaluate the relative proportions between different compounds and/or the existence of specific compounds which are used by certain manufacturers and which enable identification [4, 5, 8]. Crystal Violet (CV) is a commonly used colorant used in more than 99% of black and blue ballpoint inks, making it a universal color for any commercial brand [9].

In the original composition of the ink, in addition to Crystal Violet (CV), its two demethylated compounds are also present: pentamethylpararosaniline(Penta-PRS, Methyl Violet, MV) and tetramethylpararosaniline (Tetra-PRS) [4]. Also, in the chemical composition of blue inks of ballpoint pens of different manufacturers, in addition to CV, MV and Tetra-PRS, other dyes may be present: Aumarin (Auramine O, AuO), Rhodamine B (Rhodamine B, RhB), Ethyl Violet (EtV) and Victoria Blue B (VB) [2]. The change in the qualitative and quantitative composition of the ink after being placed on paper is influenced by the chemical composition of the ink, the type of paper and the storage conditions [3, 7, 10].

As stated by Weyermann et al. [3] and Bello de Carvalho et al. [10], it is impossible to guarantee the homogeneity of the ink applied to the paper, and the initial amount of ink applied to the paper in one stroke, i.e. the depth and width of the trace depends on the writing pressure and the diameter of the chemical ball pencils [3, 10]. Therefore, special attention should be paid to extracting a representative sample of ink from strokes on paper.

The analysis of ballpoint pen ink can be carried out by various methods of chemical analysis, and among the most commonly used is High Performance Liquid Chromatography (HPLC), which is used for qualitative and quantitative analysis of the components in the ink [1, 6]. In the HPLC method, different detectors are used, such as the DAD detector with a series of diodes (Diode-Array Detector, DAD), which is the most commonly used detector in the analysis of ballpoint pen inks. The quantitative composition of ink components analyzed by the HPLC method with a DAD detector can be expressed in several ways, and one of the ways of quantification is the estimation of the relative proportion of the components (Relative Peak Area, RPAi) by the total area method [4, 5].

The aim of this work is to characterize the inks of blue ballpoint pens using the HPLC method with a DAD detector and to determine the similarities and differences between the analyzed blue ballpoint inks from different manufacturers.

2.Experimental

2.1. Chemicals and Reagents

All chemicals and standards used were of analytical grade. Methanol, acetonitrile and trifluoroacetic acid (TFA) were purchased from Merck (USA).

Dye standards Crystal Violet (CV), Methyl Violet (MV), tetramethylpararosaniline (Tetra-PRS) and Victoria Blue B (VB) were purchased from Sigma-Aldrich (USA).

Ultrapure water with a conductivity of 0.055 µS/cm was prepared using an Elix 70 Millipore (USA) water purification system and a Genpure TKA device (Italy).

2.2. Collection and Preparation of Samples

2.2.1.Collection of Ballpoint Pen Inks Samples

For the analysis, blue ink ballpoint pens (hereinafter referred to as blue ballpoint pens) of different brands/manufacturers and different ball diameters, purchased in an office equipment and stationery store in Zagreb, were selected (Table 1).

Table 1 *Ballpoint Pen Ink Samples.*

Ballpoint pen mark	Ballpoint pen brand	Ball diameter	Country of origin
1	Aro	1 mm	Germany
2	Marvy Ushida	1 mm	Japan
3	Q-Connect	0,7 mm	Poland
4	MG	0,7 mm	China

2.2.2 Preparation of Ballpoint Pen Inks Samples

The ink samples of blue ballpoint pens (strokes with a ballpoint pen on paper) were prepared by drawing straight lines (strokes) of 10 cm with each pencil on white office paper A4 (Mondi extra 100g/m2) with the help of a ruler, and then using scissors, a 2 cm sample (of width approx. 3 mm) was cut from the line.
The cut sample (stroke, line) of 2 cm was further cut into four parts of 0.5 cm each, which were then placed in a glass test tube to which 500 µL of methanol was added. The test tube with the sample was stoppered and placed in an ultrasonic bath for 10 minutes, after which the sample was filtered and placed in a vial.

2.2.3 Preparation of Samples Paper Blanks

Clean white office paper A4 (Mondi extra 100 g/m2) was used to prepare the paper sample (paper blanks).
The sample was prepared by cutting a 10 cm long sample (approx. 3 mm wide) from a piece of A4 paper using scissors, which was then cut into 2 cm long samples (approx. 3 mm wide).
The cut sample of 2 cm was further cut into four parts of 0.5 cm each, which were then placed into a glass tube to which 500 µL of methanol was added.
The test tube with the sample was stoppered and placed in an ultrasonic bath for 10 minutes, after which the sample was filtered and placed in a vial.

2.2.4 Preparation of Standard Reference Dye Samples

Standard solutions of reference samples of dyes Crystal Violet (CV), Methyl Violet (MV), tetramethylpararosaniline (Tetra-PRS) and Victoria Blue B (VB) of different mass concentrations were prepared by dissolving in methanol.

2.3 Analytical Equipment

The analysis of standard reference dye samples and blue ballpoint pen ink samples was performed using the HPLC method with a DAD detector, and the chromatographic analysis conditions are listed in Table 2.

Table 2. *Chromatographic conditions for determination of dyes in ballpoint pen inks (method HPLC-DAD).*

Parameter	Value	
pump:	binary	
chromatographic column:	symetry C18 3,5µm (4,6x100mm)	
column temperature:	40 oC	
mobile phase A:	acetonitrile	
mobile phase B:	ultrapure water : TFA (1000mL : 0,5mL)	
pH of mobile phase A:	2,2	
injected volume:	10µL	
pressure:	max 400 bar	
detection wavelength	591 nm and 210 nm	
detector:	DAD	
time of analysis:	35 min (35 min of analysis and 3 min of stabilization)	
gradient elution program	0-29 min	60% B - 5% B
	29-34 min	5% B
	34-35 min	5% B - 60% B

2.4 Total area method

The quantification of the ink components analyzed by the HPLC method with the DAD detector was expressed by the assessment of the relative proportions of the components (Relative Peak Area, RPAi) using the total area method. The total area method calculates the relative proportion of components, i.e. the percentage of the content of a component in the mixture from the ratio of the peak area of the determined component and the total area of all peaks.

Formula for calculating the relative proportion of components using the total area method :

$$RPA_i = \frac{A_i}{A_{tot}} \times 100 \quad (1)$$

RPAi - relative proportion of the component or relative peak area of the component (Relative Peak Area, RPAi)

Ai - component peak area

Atot - total peak area of all components

3. Results and Discussion

In this work, in order to identify the dyes in blue ballpoint inks, the chromatograms and UV/VIS spectra of the analyzed standard reference dye samples were compared with the chromatograms and UV/VIS spectra of the analyzed blue ballpoint ink samples under the same analysis conditions, and the results are shown in Table 3. A sample of pure white office paper (blank) is prepared and analyzed in the same way as the ink samples of blue ballpoint pens, and thus its neutrality can be guaranteed. Table 3 shows the identified and unidentified components in blue ballpoint inks (labeled A, B, C, D, E, and F). Unidentified components are marked as A and E, and identified as B, C, D and F. It was observed that the components in the inks of the blue ballpoint pens analyzed in this paper have different retention times (tR) under the same analysis conditions, which indicates the existence of different components in ballpoint pen inks (Table 3). Components B, C, D and F were identified in the inks of the blue ballpoint pens analyzed in this work (Table 3) and it was determined that they are arylmethane dyes Crystal Violet (CV), Methyl Violet (MV), tetramethylpararosaniline, (Tetra-PRS) and Victoria Blue B (VB). In order to identify the dyes in the analyzed blue ballpoint inks, the retention times (tR) and absorbance maxima (λmax) of the components in the inks were compared with the retention times and absorbance maxima of the analyzed standard reference dyes (CV, MV, Tetra-PRS and VB). The measured values of maximum absorbance (λmax) and retention time (tR) of the analyzed standard reference dyes (CV, MV, Tetra-PRS and VB) coincide with the measured values of maximum absorbance (λmax) and retention time (tR) of the dye components (B, C), D and F) in the analyzed inks of blue ballpoint pens (Table 3). In addition, the measured values of absorbance maxima (λmax) of the analyzed standard reference dyes (CV, MV, Tetra-PRS and VB) are in accordance with the data published in the

Table 3. *Identified (B, C, D and F) and unidentified components (A and E) in ballpoint pen inks.*

Label of component in the ink	Name of the component	t_R/min	λ_{max}/nm
A	-	2,80	570
B	Tetra-PRS	3,80	574
C	Penta-PRS (Methyl Violet, MV)	4,92	584
D	Hexa-PRS (Crystal Violet, CV)	6,20	591
E	-	7,90	604
F	Victoria Blue B (VB)	9,10	617

literature [2]. Previously published literature states that Crystal Violet (CV) is a universal dye for any commercial brand of ballpoint pen because it is used in more than 99% of black and blue ballpoint pen inks, but in its original chemical composition blue ballpoint inks pencils are found along with Crystal Violet (CV) and its demethylated compounds pentamethylpararosaniline (Penta-PRS) and tetramethylpararosaniline (Tetra-PRS) [4, 9]. Also, D. Akhmerova et al. [2] state that the blue inks of ballpoint pens from different manufacturers, in addition to CV, MV and Tetra-PRS, may contain other dyes in their original chemical composition: Aumarin O (AuO), Rhodamine B (RhB), Ethyl Violet (EtV) and Victoria Blue B (VB).

By comparing the results of the qualitative analysis of the components in the inks of ballpoint pens, that is, by comparing the detected and undetected components in the inks, similarities and differences between ink samples from different manufacturers can be determined. Table 4 shows the detected (+) and undetected (-) components in the analyzed blue ballpoint inks, grouped into two groups by ball diameter (Table 1).

ink of a blue ballpoint pen marked as pen 3 (Q-Connect, ball diameter 0.7 mm), five components were detected, marked as: B, C, D, E and F, of which four components (B, C, D and F) identified as dyes (Table 3), and the presence of component A was not detected in the ink. The ink of the blue ballpoint pen marked as pen 4 (MG, ball diameter 0.7 mm) has six detected components (A, B, C, D, E and F), four components (B, C, D and F) were identified as dyes (Table 3), and one component (A) was not identified.

Blue ballpoint pens with a ball diameter of 0.5 mm (Aro and Marvy Ushida) each have six detected components and therefore it is not possible to distinguish them based on the tested qualitative chemical composition. Ballpoint pens with a ball diameter of 0.7 mm (Q-Connect and MG) have different detected components, so it is possible to distinguish them based on the tested qualitative chemical composition. The analyzed inks of blue ballpoint pens from different manufacturers (Table 1), with the same ball diameter, can be distinguished based on the tested qualitative chemical composition of the ink only if they have different detected components in the

Table 4. *Components in ballpoint pen inks (detected components are marked with a + sign, and undetected components with a – sign).*

	Label of component in the ink	A	B	C	D	E	F
Ballpoint pen mark	Ballpoint pen brand		tetra-PRS	MV	CV		VB
1	Aro	+	+	+	+	+	+
2	Marvy Ushida	+	+	+	+	+	+
3	Q-Connect	-	+	+	+	+	+
4	MG	+	+	+	+	+	+

Table 4 shows that six components (A, B, C, D, E and F) were detected in blue ballpoint inks marked as 1 and 2 (Aro and Marvy Ushida, ball diameter 1 mm), four components (B, C, D and F) were identified as dyes (Table 3), and two components (A and E) were not identified (Table 3). In the ink. However, if ballpoint pens from different manufacturers, with the same ball diameter, have the same detected ink components, then it is not possible to distinguish them based on the determination of the qualitative composition, but only on the basis of the determination of the quantitative composition [1]. Quantitative composition can be expressed in several ways, and one of the ways of quantification is the estimation of the relative proportion of the components (Relative Peak Area, RPAi) by the total area method [4, 5].

In this paper, the relative proportions of components (RPAi) in the analyzed blue ballpoint inks were calculated, and the results are shown in Table 5.

Table 5 *Relative Peak Area (RPAi) of compounds A, B, C, D, E and F in ballpoint pen inks (Undetected components with a – sign).*

Ballpoint pen mark	Ballpoint pen brand	RPAi (A)	RPAi (B)	RPAi (C)	RPAi (D)	RPAi (E)	RPAi (F)
1	Aro	0,55	7,90	37,40	40,60	2,70	10,80
2	Marvy Ushida	0,40	5,50	27,40	33,20	6,50	26,90
3	Q-Conect	/	5,80	28,90	32,85	8,90	23,50
4	MG	0,80	10,70	36,30	34,90	0,85	16,40

Table 5 shows that six components (marked as A, B, C, D, E and F) were detected in blue ballpoint inks marked 1 and 2 (Aro and Marvy Ushida, ball diameter 1 mm), and the relative proportion (RPAi) was calculated in each of the components. By comparing the relative proportions of detected components in the inks of blue ballpoint pens 1 and 2, it was determined that the relative proportions of components A, B, C and D are higher in ballpoint pen 1 than in ballpoint pen 2, and the relative proportions of components E and F are lower in ballpoint pen 1 than in ballpoint pen 2. Five components (marked as B, C, D, E and F) were detected in the ink of blue ballpoint pen 3 (Q-Connect, ball diameter 0.7 mm), and in the ink of ballpoint pen 4 (MG, ball diameter 0.7 mm), six components (A, B, C, D, E and F) were detected. The relative proportions (RPA) of the detected components in the ink of blue ballpoint pens 3 (Q-Connect) and 4 (MG) were calculated. By comparing the relative proportions of detected components in blue ballpoint pens 3 and 4, it was determined that in ballpoint pen 4 the relative proportions of components B, C and D are higher than in ballpoint pen 3, and the relative proportions of components E and F are higher in ballpoint pen 3 than in ballpoint pen 4.

The obtained quantitative results expressed as relative proportions (RPAi) of the components in the ink show that the initial concentrations of components in the inks of blue ballpoint pens manufactured by Aro (ball diameter 1 mm), Marvy Ushida (ball diameter 1 mm), Q-Connect (ball diameter 0, 7 mm) and MG (ball diameter 0.7 mm) are different and that based on the tested quantitative composition expressed through the relative proportions (RPAi) of the components, it is possible to distinguish between the analyzed inks.

4. Conclusion

Characterization of the analyzed ink samples of blue ballpoint pens manufactured by Aro (ball diameter 1 mm), Marvy Ushida (ball diameter 1 mm), Q-Connect (ball diameter 0.7 mm) and MG (ball diameter 0.7 mm) was carried out by chemical analysis of ink, i.e. by determining the chemical composition of dyes and by determining the similarities and differences in the chemical composition of detected components in the inks of blue ballpoint pens. The results show that the HPLC-DAD method used in this paper for the qualitative and quantitative analysis of blue ballpoint inks provides important information about the chemical composition of the ink, and therefore the characterization of ballpoint inks from different manufacturers can be successfully carried out based on chemical composition testing. In this paper, the total area method was used to show the quantitative composition of the components in the ink of blue ballpoint pens, which calculates the relative proportion of the component (RPAi) in the ink. On the basis of data on the qualitative (detected components) and quantitative composition of components in blue ballpoint inks (relative proportions of components), the analyzed brands of ballpoint pens manufactured by Aro, Marvy Ushida , Q-Connect and MG can be differentiated. The characterization of ballpoint pen inks based on the examination of the chemical composition of inks from different manufacturers should be continuously conducted for the purpose of creating a database that is important in forensic ink tests.

5. Reference

[1] Kher A.; Mulholland M.; Green E.; Reedy B.; Forensic classification of ballpoint pen inks using high performance liguid chromatography and infrared spectroscopy with principal components analysis and lineart discriminant analysis; Vibrational spectroscopy, Vol.40, No.2, 2006.; pp. 270-277; DOI:10.1016/j.vibspec.2005.11.002.

[2] Akhmerova D.; Krylova A.; Stavriandini A.; Shpigun O.; Rodin I.; Forensic Identification of Dyes in Ballpoint Pen Inks Using LC-ESI-MS; Chromatographia Vol.80, No.4, 2017.;pp.1701-1709; DOI:10.1007/s10337-017-3404-1.

[3] Weyermann C.; Almog J.; Bügler J.; Cantu A.A.; Minimum requiremonts for application of ink dating methods based on solvent analysis casework; Forensic Science International, Vol.210, 2011.;pp. 52-62; DOI: 10.1016/j.forsciint.2011.01.034.

[4] Diaz-Santana O.; Cardenes-Sanchez N.;Conde-Hardisson F.; Rivero_Rosales A., Suarez de Tangil Navarro M.; D.Vega-Moreno; The Use of crystal violet Degradation Products for Ballpoint Pen ink Manuscript Dating; Molecules, Vol.28, No.17, 2023.;pp.1-18; DOI: 10.3390/molecules28176429.

[5] Weyermann C.; Kirsch D.; Costa Vera C.; Spengler B.; Evaluation of the Photodegradation of Crystal violet upon Light Exposure by Mass Spectrometric and Spectroscopic Methods; Journal of Forensic Sciences, Vol.54, No. 2, 2009.; pp.339-345; DOI: 10.1111/j.1556-4029.2008.00975.x.

[6] Halim M. I. A.; Saim N.; Osman R.; Jasmani H.; Abidin N.N.Z.; Discrimination of black ballpoint pen inks by High performance liquid chromatography (HPLC); The Malaysian Journal of analytical Sciences, Vol.17, No.2, 2013.; pp.230-235; ISSN 1394-2506.

[7] Huan-Yung F.; Shiuh-Tsuen H.; Wen-Hsin C.; Jeng-Lyan J.; Wan-Yu L.; Chiing-Chang C.; Degradation pathways of crystal violet by Fenton and fenton –like systems: Condition optimization and intermediate separatio and identification; Journal of Hazardous Materials, Vol. 171, No.1-3, 2009.; pp.1032-1044; DOI:10.1016/j.jhazmat.2009.06.117

[8] Ortiz-Herrero L.; de Almeida Assis A.C.; Bartolome L.; Alonso M.L.; Maguregui M. I.; Alonso R.M.; Seixas de Melo J.S.; A novel, non-invasive, multi-purpose and comprehensive method to date inks in real handwritten documents based on the monitoring of the dye ageing processes; Chemometrics and Intelligent Laboratory Sistem; Vol.207, 2020.; pp.104187; DOI:10.1016/j.chemolab.2020.104187.

[9] Deviterne-Lapeyre C.M.; Interpol Review of Questioned Documents 2016-2019; Forensic Science International: Synergy; Vol.2, 2020.; pp.429-441 DOI: 10.1016/j.fsisyn.2020.01.012

[10] Bello de Carvalho C.; Ortiz R. S.; dos Reis M.; Zamboni A.; Limberger R.P.; Ferrao M.F.; Vaz B.G.; Characterization and Differentation of Ballpoint Pen Inks Strokes on Paper Using Orbitrap Mass Spectrometry and Multivariate Statistic; Forensic Science & Addiction Research, Vol.2, 2018.; pp.1-8; DOI:10.31031/FSAR.2018.02.000537.