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الجمعية العربية لعلوم الأدلة الجنائية والطب الشرعي
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Original Article

Differentiation of Red and Black Ballpoint Pen Inks using High Performance Thin Layer Chromatography and Gas Chromatography-Mass Spectrometry

تمييز أحبار الأقلام الجافة الحمراء والسوداء باستخدام كروماتوغرافيا الطبقة الرقيقة عالية الأداء والكروماتوغرافيا الغازية المقترنة بمطياف الكتلة

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Abstract

The questioned document examiners usually encounter cases related to handwritten documents for the determination of their source, origin, and authenticity. The legal documents usually involve handwriting or signatures executed using ballpoint pens. These components of the ballpoint pen inks can be analysed, both qualitatively and quantitatively, using several techniques. The present study aimed to analyse the red and black ballpoint pen inks using high performance thin layer chromatography and gas chromatography-mass spectrometry techniques. All samples have been completely differentiated using high performance thin layer chromatography. The discrimination potential of gas chromatography-mass spectrometry for red and black ballpoint pen inks was found to be 32.85% and 63.58% respectively. Classification of inks has been performed in two levels, that is, primary differentiation on the grounds of major components of the ink and subsequent differentiation on the basis of minor components. The validity of technique was tested in terms of repeatability and reproducibility. Reproducibility has been determined by repeating the procedure of repeatability on different days. The results have been evaluated in terms of relative standard deviation (RSD), which is <2% for both repeatability and reproducibility.

Keywords: *Forensic Sciences, Questioned Document, Differentiation, Ball Point Pen Inks, HPTLC, GC-MS.*

المستخلص

يواجه المحققون عادة بعض الحالات المرتبطة بالوثائق التي تحتوي كتابات بخط اليد مع ضرورة تحديد مصدرها وأصلها وصحتها، وغالباً ما تتضمن الوثائق القانونية كتابات بخط اليد أو تواقيع مكتوبة بقلم الحبر الجاف، ويمكن تحليل مكونات أحبار الأقلام الجافة كمياً ونوعياً باستخدام عدة طرق.

تهدف هذه الدراسة إلى تحليل أحبار قلم الحبر الجاف باللونين الأحمر والأسود باستخدام تقنيتي كروماتوغرافيا الطبقة الرقيقة عالية الأداء والكروماتوغرافيا الغازية المقترنة بمطياف الكتلة، وقد تم التفريق التام بين جميع العينات باستخدام كروماتوغرافيا الطبقة الرقيقة عالية الأداء، بينما كانت إمكانية التمييز بواسطة الكروماتوغرافيا الغازية المقترنة بمطياف الكتلة لأحبار قلم الحبر الجاف الأحمر والأسود بنسبة 32.85%، و63.58% على التوالي. وصنفت الأحبار على مستويين: التمييز الأولي عن طريق المكونات الأساسية، والتمييز اللاحق باستخدام المكونات الثانوية. تم اختبار صلاحية التقنية من حيث قابلية التكرار على مدى يوم واحد وعدة أيام. وقيّمت النتائج بواسطة الانحراف المعياري النسبي والذي كان أقل من 2% لكل من قابلية التكرار على مدى يوم واحد وعدة أيام.

الكلمات المفتاحية: علوم الأدلة الجنائية، الوثائق محل التحقيق، التمييز، أحبار الأقلام الجافة برأس كروي، HPTLC, GC-MS.

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1. Introduction

Most legal documents such as financial wills, property deeds, bank cheques, application forms, etc., involve handwriting or signatures of related individuals. Thus, handwritten documents attain high significance despite the widespread use of printed documents. Questioned document examiners usually encounter cases related to handwritten documents for the determination of their source, origin, and authenticity.

Legal documents usually involve handwriting or signatures made using ballpoint pens. Most ballpoint pen inks are a homogenous mixture of dye-based colourants, glycol based solvents, and several additives. These components can be analysed both qualitatively and quantitatively through chromatographic [1-3] and spectroscopic techniques [4-9] or a combination of both. According to a survey, spectroscopic techniques are more often used for the analysis of inks [10]. This is because of their high sensitivity and minimum damage to documents. The result obtained from these techniques is more reliable and objective. Some spectroscopic techniques like inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES) are destructive in nature [11]. Also, these spectroscopic techniques are highly expensive and demand high maintenance. Therefore, these techniques are not favoured for routine caseworks. In such cases, the examiner has to rely on a combination of techniques which are commonly available and demand minimal sample preparation. High-performance thin layer chromatography (HPTLC) and GC-MS are two of those techniques. They are used to analyze drugs, explosives, inks, and petroleum products, etc.

HPTLC reported high discrimination potential to differentiate blue, black and red ballpoint pen inks manufactured in Malaysia and Romania [12-15]. GC-MS is another efficient tool that discriminates inks on the basis of their non-coloured components such as their solvents and additives. It was employed to differentiate two red pilot ballpoint pen inks manufactured in 1998 and 1999 [16]. The combined use of TLC and GC-MS has solved two actual cases of alteration. Several research works have reported the characterization of blue ballpoint pen inks manufactured in different parts of the world [17-20]. However, very limited research has been conducted to differentiate the ballpoint pen inks of other colours, such as red and black. Thus, the present study was aimed at analysing red and black ballpoint pen inks of Indian origin using HPTLC and GC-MS techniques. This study also verifies the validity of the used techniques in terms of repeatability and reproducibility.

2. Materials and Methods

A total of 78 ballpoint pens including 40 red and 38 black pen inks were acquired from local stationary shops in India (Table-1). The collected pens were each marked with a unique sample identification code. Each pen was used to write the phrase "FORENSIC SCIENCE" multiple times on A4 sheets. Each prepared sheet was placed in separate envelopes and stored in closed cabinets at normal room temperature. Two discs (1 mm diameter) of ink strokes were punched from each prepared sheet using a metal handheld puncher and were then dissolved in 30 μL of HPLC grade methanol (Loba Chemie, Pvt. Ltd, India). Blank paper and reference dyes dissolved in methanol were considered as standard samples.

Table 1- *Description of ball point pens examined.*

Red ball point		Black ball point	
Make/Model	**Sample ID**	**Make/Model**	**Sample ID**
Reynolds/Fusion	R1	Steadtler/----	BL1
Revynolds/Champ	R2	Elkos/Better	BL2
Reynolds/B and B	R3	Linc/Glycer	BL3
DANA air crash	R4	Montex/Mega Top	BL4
Cello/4 color	R5	Montex/Presto	BL5
Reynolds/Brite	R6	Montex/Tressa	BL6
Elkos/Better	R7	Pentek/Fino color	BL7
Linc/Glycer	R8	Flair/Xtramile	BL8
Steadtler/----	R9	Flair/Jackpot	BL9
Montex/Tressa	R10	Flair/Ezee click	BL10
Montex/ Winner	R11	Flair/FX	BL11
Montex/Presto	R12	Cello/4 color	BL12
Montex/Megatop	R13	Reynolds/B and B	BL13
Pentek/Fino color	R14	Reynolds/Liquiflo	BL14
Flair/Xtramile	R15	Reynolds/Brite	BL15
Flair/Jackpot	R16	Reynolds/Fusion bold	BL16
Flair/Q5	R17	Goldex/Klassy	BL17
Flair/Fx	R18	Goldex/Klear	BL18
Flair/Ezeeclick	R19	Goldex/Checkmate	BL19
Flair/Sharpoint	R20	Flair/Sunny	BL20
Flair/Charger	R21	Flair/Q5	BL21
Goldex/Klassy	R22	Flair/Marathon	BL22
Goldex/Checkmate	R23	Flair/Ezeeclick	BL23
Goldex/Klear	R24	Reynolds/Liquiflo	BL24
Cello/2x	R25	Reynolds/BandB	BL25
Cello/Butterflow	R26	Pentel/Slimgrip	BL26
Cello/Trimate	R27	Steadtler/----	BL27

Continued on the next page

Table 1- *(continued)*

Cello/Liquiball	R28	Cello/Winner	BL28
Cello/Zipper	R29	Linc/Glycer	BL29
Cello/Maxwriter	R30	Flair/Surfer	BL30
Montex/Smoothflow	R31	Goldex/Klear	BL31
Flair/Airbalance	R32	Flair/2 color	BL32
Montex/18UP	R33	Cello/MaxwriterXs	BL33
Reynolds/Champ	R34	Cello/Tripus	BL34
Reynolds/Fine carbure	R35	Cello/Winner	BL35
Cello/Quick	R36	Reynolds/Champ	BL36
Cello/Mayfair	R37	Cello/Pinpoint Xs	BL37
Pentel/Slimgrip	R38	Montex/Winner	BL38
Flair/Sunny	R39		
Flair/Silkflow	R40		

2.1 HPTLC Method

The samples were analysed using a HPTLC unit (CAMAG, Switzerland) equipped with a sample applicator and TLC scanner. About 10 μL of each prepared ink sample was spotted on HPTLC silica gel plates (Merck, Germany) of dimension 6.5 × 20 cm with the help of a Camag Linomat IV spot applicator. The parameters such as sample volume, position of bands, band width, distance between relative bands, and scanning range were controlled by Win Cat Software installed on a personal computer. The syringe was washed twice with methanol after each application to remove any existing traces of previous ink samples. The spotted chromatograms were then allowed to develop in two solvent systems, i.e. ethyl acetate: ethanol: distilled water (70:35:30) (solvent system I) and n-butanol: ethanol: distilled water (50:10:15) (solvent system II). The developing time for both the solvent systems was 25 minutes and 50 minutes, respectively. The developed plates were then visualised under daylight under 254 nm ultraviolet illumination. The results were primarily interpreted on the basis of differences in hRf value of spots under daylight and ultraviolet illumination. The remaining undifferentiated samples of primary analysis were then examined for the presence of additional spots at 585 nm, 540 nm, 425 nm, 415 nm, and 366 nm (in the ultraviolet region).

2.2 GC-MS Method

The analysis of the methanol ink extracts no older than 1 month was performed using a Shimadzu GC-MS QP2010 Ultra interfaced with an AOCi auto injector. The column incorporated within GC was Rtx5sil MS (midpolar-1, 4bis (dimethylsiloxy) phenylene dimethyl polysiloxane) of dimension 30 m × 0.25 mm × 0.25μm. Other parameters included Helium as carrier gas: column flow of 1.40 mL

/min, injection volume of 3 μL splitless at 220 °C temperature, oven programme with isothermal for 1 °C to 40 °C hold for 0.35 minutes; 10 °C/min to 220 °C hold for 5 minutes, and 10°C/min to 250 °C hold for 5 minutes; transfer line temperature of 280 °C, solvent delay of 3 min and scan range of 39-400 a.m.u.

3. Results

Seventy-eight red and black ballpoint pen ink samples were analysed using HPTLC and GC-MS.

3.1 HPTLC

3.1.1 Analysis of red ballpoint pen inks

In solvent system I, 40 red ballpoint pen inks were classified into four groups (Group 1-Group 4) on the basis of the difference in number, colour and hRf value of dye under visible and ultraviolet illumination. Rhodamine 6G (R6G) was found to be the major dye among red ballpoint pen inks. A few ink samples showed a pink colour band for Rhodamine B (RB) in visible light but did not emit fluorescence under ultraviolet illumination. This difference was observed in samples R32 and R38 (Figure-1). It clearly indicated the presence of a kind of pink dye in R32, showing very close hRf to Rhodamine B. Similar findings were reported by previous researchers [12]. The samples were then subjected to a TLC scanner at 540 nm, 425 nm and 366 nm. The presence of additional spots classified red ballpoint pen inks into five groups at 540 nm, eight groups at 425 nm and five groups at 366 nm. Therefore, 26 out of 40 samples were completely differentiated in Solvent System I. The remaining non-differentiated samples were successfully distinguished in Solvent System II (Figure-2).

3.1.2 Analysis of black ballpoint pen inks

In solvent system I, 38 black ballpoint pen inks were classified into six groups (Group 1-Group 6) on the basis of difference in number, colour and hRf value of dyestuff components under visible and ultraviolet illumination. Crystal violet and metanil yellow were found as major dyestuff components among black ballpoint pen inks (Figure-3). The samples were then subjected to TLC scanner at 580 nm, 415 nm, 540 nm, and 366 nm. The presence of additional spots led to the classification of black ballpoint pen inks into nine groups at 580 nm, five groups at 540 nm and ten groups at 366 nm. No differentiation was achieved at 415 nm. Therefore, 28 out of 40 samples were completely differentiated in Solvent System I. The remaining non-differentiated samples were successfully differentiated in Solvent System II (Figure-4).

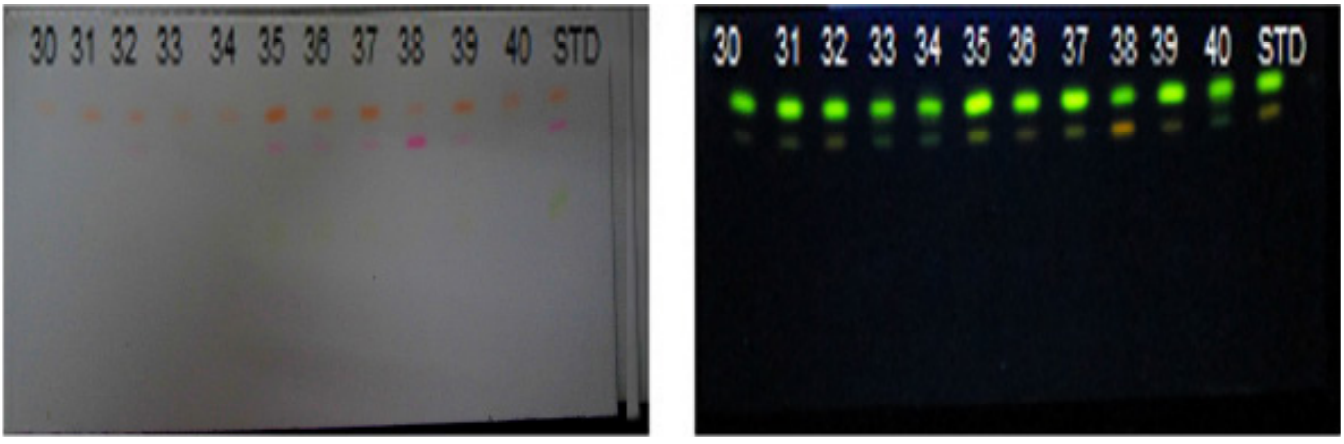

Figure 1- *HPTLC profile of red ball point pen inks (R30-R40) under visible light and ultraviolet light in solvent system I.*

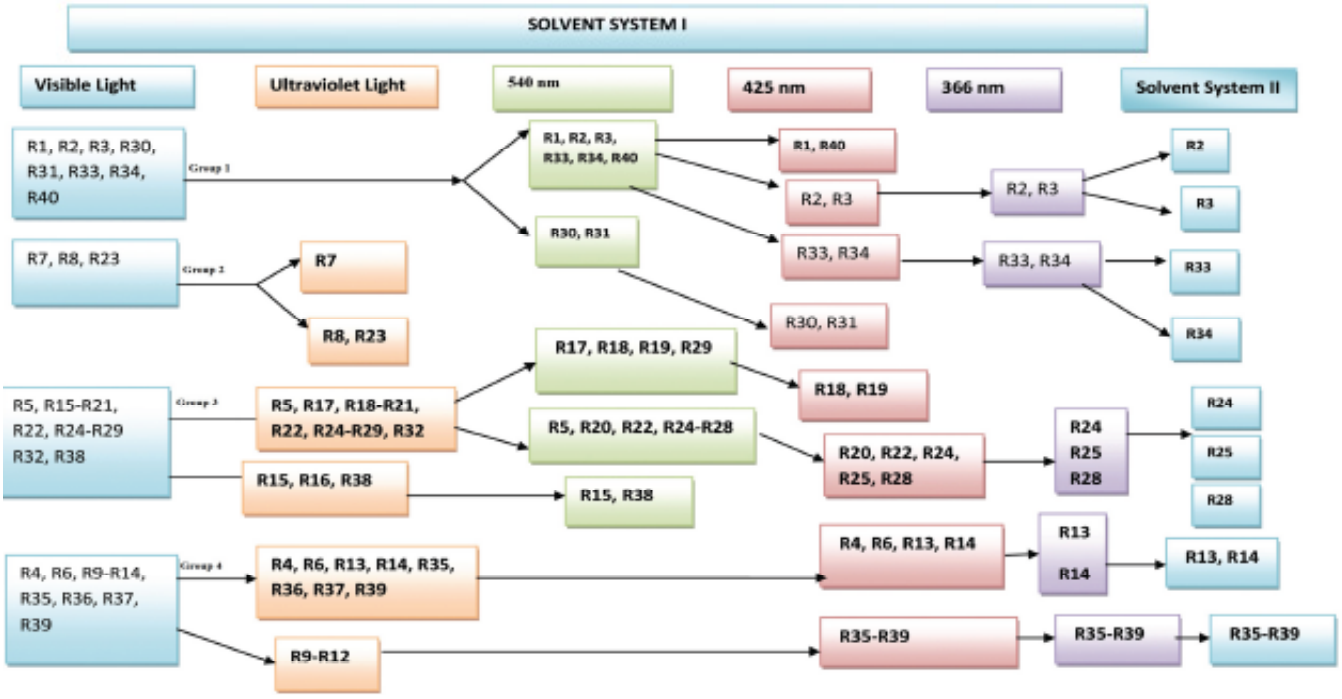

Figure 2- *Schematic presentation of differentiation of red ball point pen inks in solvent I and solvent system II.*

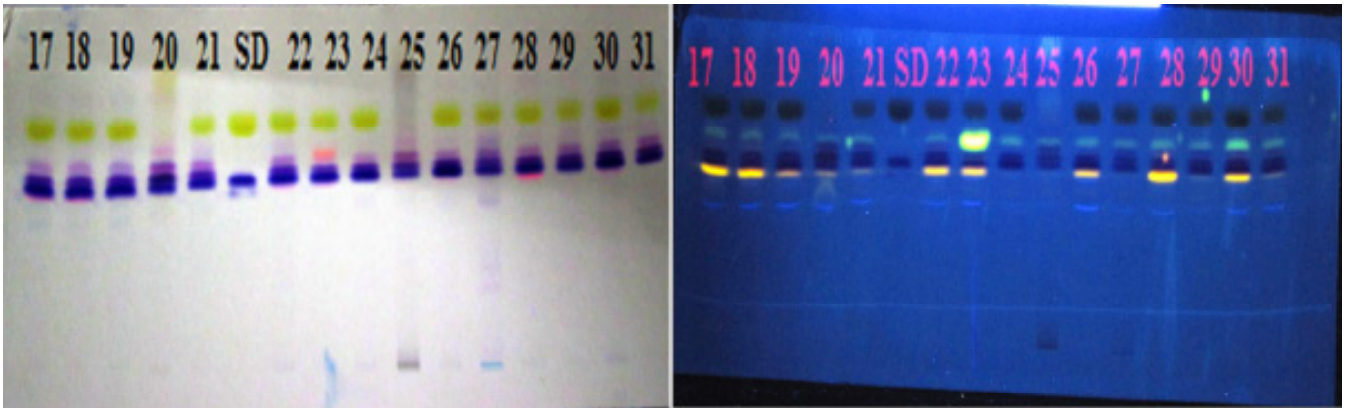

Figure 3- *HPTLC profile of black ball point pen inks (BL17-BL31) under visible light and ultraviolet light in solvent system I.*

3.2 GC-MS

3.2.1 Analysis of red ballpoint pen inks

Total ion chromatogram of red ballpoint pen inks is shown in Figure-5. Forty red ballpoint pen inks were classified into five groups (Group 1-Group 5) on the basis of their major components, i.e., 2 phenoxyethanol (2PE), benzyl alcohol and 1, 3 dimethylbenznene. For example, Group 3 consisting of 10 samples (R9, R26, R29, R31, R32, R35, R36, R37, R39 and R40) had 2PE and benzyl alcohol as major volatile components. Further classification was done on the basis of minor components that were specific to individual ink samples (Table-2). This led to the differentiation of all the ink samples in Group 3 except R36 and R39. A similar methodology was followed to differentiate the remaining groups. A total of 32 out of 40 samples were completely differentiated on the basis of major and minor components.

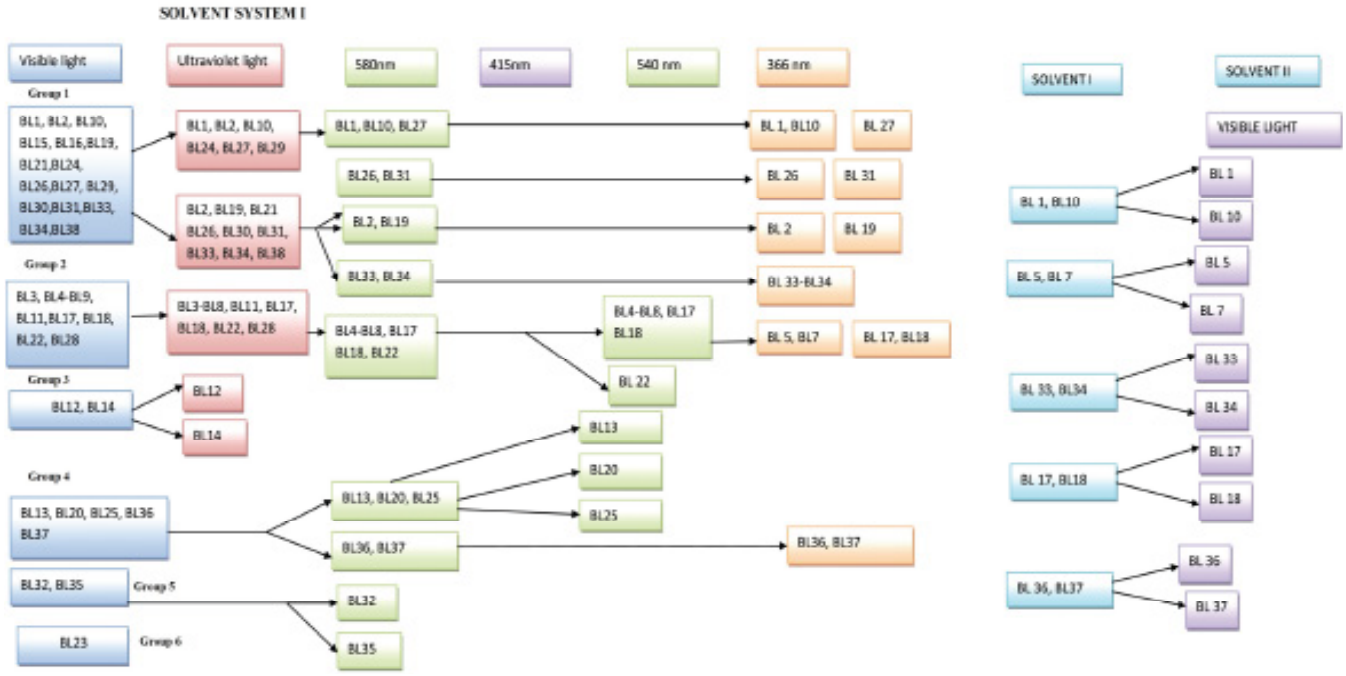

Figure 4- *HPTLC profile of black ball point pen inks (BL17-BL31) under visible light and ultraviolet light in solvent system I.*

3.2.2 Analysis of black ballpoint pen inks

Total ion chromatogram of black ballpoint pen inks is shown in Figure-6. Thirty-eight black ballpoint pen inks were classified into 6 groups (Group 1-Group 6) on the basis of their major components. These components included 3, 3 dimethoxybutanone, 1, 1 diisopropoxypropane, diisopropyl propional, and 2 PE. For example, Group 6 consisting of 7 samples (BL 8, BL10, BL22 BL23, BL30, BL33 and BL37) had 3, 3 dimethoxybutanone and 2PE as their major components. Further classification was done on the basis of minor components that were specific to individual ink samples (Table-3). This led to the differentiation of all ink samples in Group 6, except BL 33. A similar procedure was followed to differentiate the remaining groups. Out of 38 samples, 22 samples were completely differentiated on the basis of major and minor components.

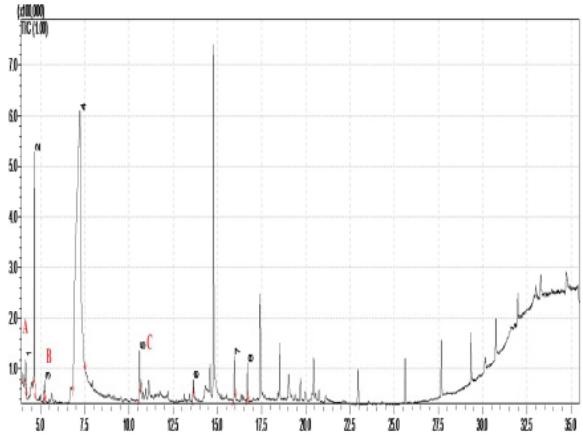

Figure 5- *Total ion chromatogram of red ball point pen ink (R8) representing (A) 2 mercapto ethanol (B) 1,2,3 propanetriol (C) Pentanoic acid, methyl ester.*

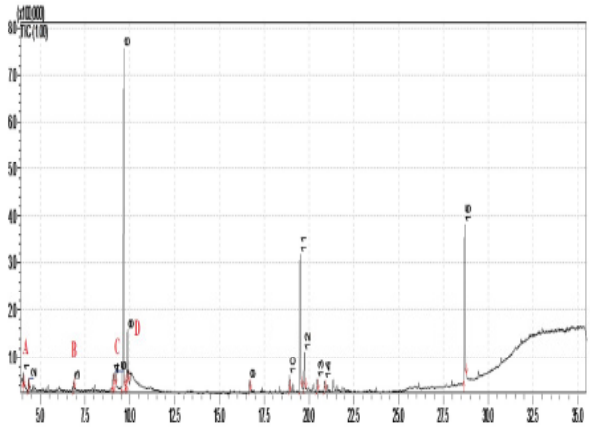

Figure 6- *Total ion chromatogram of black ball point pen ink (BL 23) representing (A) 3,3 dimethoxy-2-butanone (B) 2 ethyl hexanol (C) 3 (hydroxyl-phenyl-methyl) 2,3 dimethyl octan-4-one (D) 2 Phenoxyethanol.*

Table 2- *List of components identified in red ball point pen inks.*

Groups (*n*)	Major Components	Sample Id	Minor Components	RT (mins)
Group 1 (*n*=13)	2-Phenoxyethanol	R6	Trimethylsilyl ester	16.695
		R7	1,2-Benzisothiazol-3-amine Tbdms	31.5
		R 10	Hexanoic acid, 6 amino	11.72
		R 11	3,3-dimethoxy-2-butanone	4.129
		R 13	Dibutylamine n-ethyl	10.881
		R 15	1,3-pentadiene, 2 methyl	7.06
		R 19	----------	----------
		R 20	1,2-Bis (trimethylsilyl) benznene	31.865
		R 28	----------	----------
		R 30	2-Pyridine carboxylic acid, 6 amino	11.39
		R 33	4-methyltetrahydropyran	4.335
		R 34	----------	--------
		R 38	Methyl valerate	4.539
Group 2 (*n*=1)	Benzyl alcohol	R 17	Benzyl alcohol	5.222
Group 3 (*n*=10)	2-Phenoxyethanol Benzyl alcohol	R 9	1,2,3-Propanetriol	6.994
		R 26	Methyl-6-hydroxycaproate	4.477
		R 29	Cyclopentene 1-methyl	7.068
		R 31	4-methyl tetrahydropyran	4.335
		R 32	Pentalene, octahydro-cis-	7.064
		R 35	Benzene, 1,3-dimethyl	5.641
		R 36	--------	-------
		R 37	2-ethyhexyl salicylate	19.045
		R 39	----------	---------
		R 40	1,4-butanediol	16.17
Group 4 (*n*=1)	2-Phenoxyethanol Benzyl alcohol 1,3-dimethyl benzene	R 24	2-Phenoxyethanol	10.756
			Benzyl alcohol	5.218
			1,3-dimethyl benzene	5.638
Group 5 (*n*=6)	2-Phenoxyethanol 1,3-dimethyl benzene	R 1	1,2-Benzenediol	4.005
		R 2	Benzaldehyde	6.638
		R 3	1-Hexanal, 2-ethyl	7.611
		R 4	1-heptanol	4.31
		R 5	Methyl-6-hydroxycaproate	4.469
		R 27	2-Propanol 1'1 Oxybis	7.805

Table 3- *List of components identified in black ball point pen inks.*

Groups (*n*)	Major Components	Sample Id	Minor components	RT (mins)
Group 1 (*n*=13)	3,3-dimethoxy-2-butanone	BL 2	----------	----------
		BL 5	----------	----------
		BL 7	Nonane, 5-Butyl	9.087
		BL 17	3-pentanone, 2,4-dimethyl	3.949
		BL 18	Hexadecanoic acid, methyl ester	19.11
		BL 19	2-Ethylhexyl salicylate	17.803
		BL 20	Pentanoic acid, 2-methyl-methyl ester	4.366
		BL 24	----------	----------
		BL 27	----------	----------
		BL 28	----------	---------
		BL 31	----------	---------
		BL 32	----------	----------
		BL 35	----------	----------
Group 1 (*n*=13)	3,3-dimethoxy-2-butanone	BL 1	1-hexanol 2-ethyl	6.868
		BL 4	---------	----------
		BL 13	----------	----------
		BL 14	----------	----------
		BL 15	----------	----------
		BL 21	Hexadecanoic acid, methyl ester	19.102
		BL 25	Undecane 3-methyl	9.183
		BL 36	Tert butyl (dimethyl) silyl propionate	5.442
Group 3 (*n*=2)	2-Phenoxyethanol	BL 26	--------	----------
		BL 38	1 Iodo-2-methylnonane	9.071
Group 4 (*n*=1)	3,3-dimethoxy-2-butanone 1,1-Diisopropoxypropane, diisopropyl propional	BL 16	3,3-dimethoxy-2-butanone 1,1-Diisopropoxypropane, diisopropyl propional	
Group 5 (*n*=1)	1,1-Diisopropoxypropane, diisopropyl propional 2 Phenoxyethanol	BL 3	1,1-Diisopropoxypropane, diisopropyl propional 2-Phenoxyethanol	9.071 4.079 9.834
Group 6 (*n*=7)	3,3-dimethoxy-2-butanone 2-Phenoxyethanol	BL 8	Benzoic acid, 2,6-Bis (trimethylsiloxy)-trimethyl silyl ester	15.6
		BL 10	Nonane 5-butyl	9.086
		BL 22	1-hexanol 2-ethyl	6.864
		BL 23	1-iodo-methylnonane	9.084
		BL 30	--------	----------
		BL 33	Undecane 3-methyl	9.177
		BL 37	Phenoxyethanol	834

4. Discussion

Previous studies have not reported such a wide range of components in ballpoint pen inks using GC-MS. Certain components such as dodecane, 1, 2 benzenedicarboxylic acid; 1, 2 benzenedicarboxylic acid bis (2 methylpropyl) ester; 1, 2 benzenedicarboxylic acid, butyl octyl ester; 1, 2 benzenedicarboxylic acid, dioctyl ester; 1, 2 benzenedicarboxylic acid, butyl methyl ester; 1, 2 benzenedicarboxylic acid bis (2 methylpropyl), pentanoic acid, methyl ester; butanoic acid, methyl ester were found in both ink and paper samples. Therefore, these components have not been considered during the evaluation of results. Few components have been found to be specific for each ink colour. For example, 5 butyl nonane, 3 pentanone 2,4 dimethyl, 1 iodo-2 methylnonane have been found in black ink colour samples only.

5. Repeatability, Reproducibility and Discrimination Potential (DP)

The validity of the above technique was proved by studying its repeatability and reproducibility. Repeatability was determined by analysing the chosen ink samples using HPTLC and GC-MS nine times. Reproducibility was determined by repeating the procedure of repeatability on 3 different days. The results were evaluated in terms of relative standard deviation (RSD), which is <2% for both repeatability and reproducibility (Table-4).

Discrimination potential is defined as the ability of technique to differentiate red and black ballpoint pen inks. It is calculated as:

$$DP = \frac{\text{Number of discriminated pairs x 100}}{\text{Number of possible pairs}}$$

Here, the number of pairs calculated = n (n-1)/2

Table 4- *Validation of HPTLC in terms of repeatability and reproducibility.*

Number replicates	Repeatability		Reproducibility	
	R15 (R6G)	R24 (RB)	R15 (R6G)	R24 (RB)
1	70	63	69	64
2	69	64	68	63
3	68	64	70	64
4	68	64	68	64
5	69	63	69	61
6	70	62	68	62
7	70	62	70	63
8	68	61	69	62
9	68	64	69	61
R.S.D	**1.35**	**1.77**	**1.13**	**1.95**

A previous study reported 77.27% discrimination potential of HPTLC in differentiating red ballpoint pen inks [12]. In the present study, complete differentiation has been achieved by HPTLC. Similarly, the potential of GC-MS in differentiating red and black ballpoint pen inks has been found to be 32.85% and 63.58%, respectively. This difference may have occurred due to the diversity of components added to black inks as compared to the red ballpoint pen inks. The high discrimination potential of both techniques makes them reliable for the analysis of ink evidence encoutered in various types of civil and criminal cases.

6. Conclusion

HPTLC and GC-MS were found to be efficient techniques in discriminating 40 red and 38 black ballpoint pen inks of Indian origin. All the samples were completely differentiated using HPTLC. GC-MS discriminated red and black ballpoint pen inks with discrimination potential of 32.85% and 63.58%, respectively. Classification of inks was performed on two levels, i.e. primary differentiation on the grounds of major components and subsequent differentiation on the basis of minor components. Maximum differentiation was achieved on the basis of minor rather than major components. The techniques were tested in terms of repeatability and reproducibility for R15 and R24. The obtained results will hopefully assist questioned document examiners in the analysis of alterations in real case scenarios. Future research may involve the analysis of different types of inks and their colours.

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Conflict of Interest

None.

Source of Funding

None.

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