



Differentiation of Inkjet Printer Inks by Thin Layer Chromatography and High Performance Thin Layer Chromatography

Saini Komal*, Heer Harinder Kaur and Rathore Rajshree
Department of Forensic Science, Punjabi University, Patiala, 147002, INDIA

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Abstract

In this study, 20 colored inkjet ink samples (both original and refilled) were analyzed on the basis of their dye components by using thin layer chromatography (TLC) and high performance thin layer chromatography (HPTLC). Dyestuffs in the inks were extracted using ethanol and picric acid. Two solvent systems were found efficient to differentiate the all colored inkjet ink samples. TLC and HPTLC differentiated all the ink samples.

Keywords: High Performance, thin layer chromatography, questioned documents, inkjet inks.

Introduction

Inkjet printers are the most commonly used printing devices available in the market these days. Their widespread use, easy availability, multifunctional purpose and affordable prices have reduced the efforts of forgers in altering certificates, counterfeiting bank notes etc. Forensic document examiners (FDEs) are often asked to prove the authenticity of documents related to such cases¹. Ink examination plays a significant role in proving whether the inks are similar or dissimilar. Inks are comprised of three major components: – coloring matter, solvent and binder along with various additives such as dryers, dispersants or UV-blockers². Colorants such as dyes are widely used for the differentiation and comparison of inks. Inkjet printer cartridges are filled with original inks as well as refilled inks. When refilled inks are added to the existing original cartridge, they may alter the composition of the original or refilled ink³. Therefore, it becomes very important to differentiate them. Thin layer chromatography (TLC) is the most preferred separation technique as it is inexpensive and easy to perform^{4,6}. High performance thin layer chromatography (HPTLC) is also rapid and reproducible technique, which helps in the comparison and identification of the inks⁷⁻⁹. Limited research has been carried out to analyze the differentiating ability of HPTLC. In the present study, both original and refilled inkjet inks have been analyzed using TLC and HPTLC on the basis of dye components.

Material and Methods

Sample Collection: Twenty (20) samples of colored inkjet ink cartridges (both original and refilled) of different make and models were collected and marked serially (table-1).

Table-1
Ink Samples Collected from Different Inkjet Printers

Sample no.	Printer	Model no.	Ink
1	Brother	MFC-J430W	Refilled
2	HP	J125	Refilled
3	HP	-	Refilled
4	HP	-	Refilled
5	Brother	-	Refilled
6	Brother	J430	Refilled
7	Epson	-	Refilled
8	HP	-	Original
9	Brother	-	Original
10	Brother	625W	Refilled
11	Brother	DCPJ125	Refilled
12	Epson	L210	Original
13	Brother	J1255	Refilled
14	HPK Office	Jet Pro K 5300	Original
15	HP Office Jet	Pro K 5300	Refilled
16	Epson	R230	Refilled
17	Brother	DCP-J125	Refilled
18	HP	F2235	Refilled
19	Epson	L210	Refilled
20	HP	B9180	Refilled

Sample preparation: Small volume (0.5 mL) of each of four colors, that is, cyan, magenta, yellow and black (CMYK) of inkjet ink were extracted using a syringe (3 mL hypodermic syringe) from four different chambers of an ink cartridge. 0.1 mL of each of four color inks extract was then poured and mixed in another sampling vial. This was done because cyan, magenta, yellow and black (CMYK) are used for printing the picture in layers. Hence the four colored inkjet inks have to be analyzed and considered as a mixture¹⁰. The same process was done for all twenty inkjet inks samples, which then were labeled and documented. Ethanol was used to extract the dye components present in the prepared mixture. 0.1 mL of the mixture extract was dissolved in ethanol (5 mL). However, some black and yellow samples were partially soluble in ethanol. Aginsky¹¹ used dimethylformamide (DMF) and sulphuric acid (H₂SO₄) to dissolve all the organic pigments present in the inks. In the present study, an attempt has been made to use picric acid (saturated aqueous solution, laboratory reagent, s.d. fine-chem limited, Mumbai, India) to dissolve the inkjet inks. Picric acid (aqueous solution) is highly soluble in water. It was found efficient to dissolve all the ink samples. So, both ethanol and picric acid were used separately to extract dye components of all the ink samples.

All twenty inkjet ink samples were extracted separately with ethanol as well as picric acid. In total 20+20= 40 samples have been studied for ink examination by using TLC and HPTLC techniques.

Solvent and Stationary Phase: The chemicals such as ethanol, ethyl acetate, distilled water and n-butanol were used in the study. All reagents were of laboratory reagent grade and have been purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Saturated aqueous solution of picric acid was used as an extraction solvent, which was of laboratory reagent grade and was procured from s.d. fine-chem limited, Mumbai, India. Extracted ink samples (original and refilled) were analyzed with TLC and HPTLC separately. Five solvent systems were tried, out of which two (table-2) (code I and II) were found most suitable to analyze all the ink samples by TLC and HPTLC. Selected solvent systems were kept in two separate chambers for saturation for one hour at room temperature. Precoated TLC (silica Gel 60 F254, Merck) plates without fluorescence were used as stationary phase for both the techniques.

Thin layer chromatography (TLC): Spotting of extracted samples and visualization of spots: The mixture extract of four colors (CMYK) of inkjet inks (both original and refilled) were spotted manually on precoated silica gel 60 (F254 Merck) TLC plates with the help of fine capillary tubes (outer diameter 1.36 mm, thickness 0.01 mm and internal diameter 1.34 mm). Spotted TLC plates were placed in an oven at 95°C for 3 minutes to remove the extraction solvent which were then cooled at room temperature. Spotted precoated TLC plates were placed vertically in the chamber and were then allowed to run

up to 5 cm.

Table-2

Solvent Systems Used for Thin Layer Chromatography and High Performance Thin Layer Chromatography of Inks of Color Inkjet Printers

Solvent System Codes	Solvent Systems	Ratio
I	Ethyl acetate: Ethanol: Distilled water	70: 35: 30
II	n-Butanol: Ethanol: Distilled water	90: 15: 10

The developed TLC plates after drying at room temperature were observed in the visible light. They were then exposed to short wave and long wave ultraviolet light in order to record the color and fluorescence of the developed spots. The hR_f value of each spot was calculated and tabulated.

High performance thin layer chromatography (HPTLC): Prepared mixture extract (0.2 µL) of all inkjet inks (both original and refilled) was taken out from the vial using a micrometric glass syringe (100 µL). The syringe was fixed to an automatic TLC sampler (ATS4). The parameters like sample volume, bandwidth, developing and extraction solvent were all controlled by HPTLC software (win CATS). The sample was sprayed in the form of bands on the precoated TLC plate. After every application, the syringe was washed twice with methanol to remove the traces of previous ink sample. Spotted precoated TLC plates were dried for 15-20 minutes at normal room temperature. Dried TLC plates were placed vertically in the chamber.

The developed chromatograms were allowed to dry at room temperature and were observed in the visible light. They were then exposed to short wave and long wave ultraviolet light to record the color and fluorescence of the developed spots. The hR_f value of each spot was obtained automatically. For better separation and resolution, developed chromatograms were scanned under TLC Scanner in absorption visible mode at 520 nm wavelength. Images of the chromatogram were documented using Digistore documentation system. Results obtained were digitally stored in the form 3D graphs (figure-1).

Interpretation of Results: hR_f value of all the spots was calculated as

$$hR_f = \frac{\text{Distance travelled by solute (spot)} \times 100}{\text{Distance travelled by the solvent front}}$$

Analysis by thin layer chromatography: The solvent systems I and II were found most suitable for the separation of the dye components. The mixture extract of all the inkjet inks was spotted manually on precoated TLC plates and the results were obtained. The results of all the samples were interpreted on the basis of differences in their number, color and hR_f value of spots

under visible and UV light.

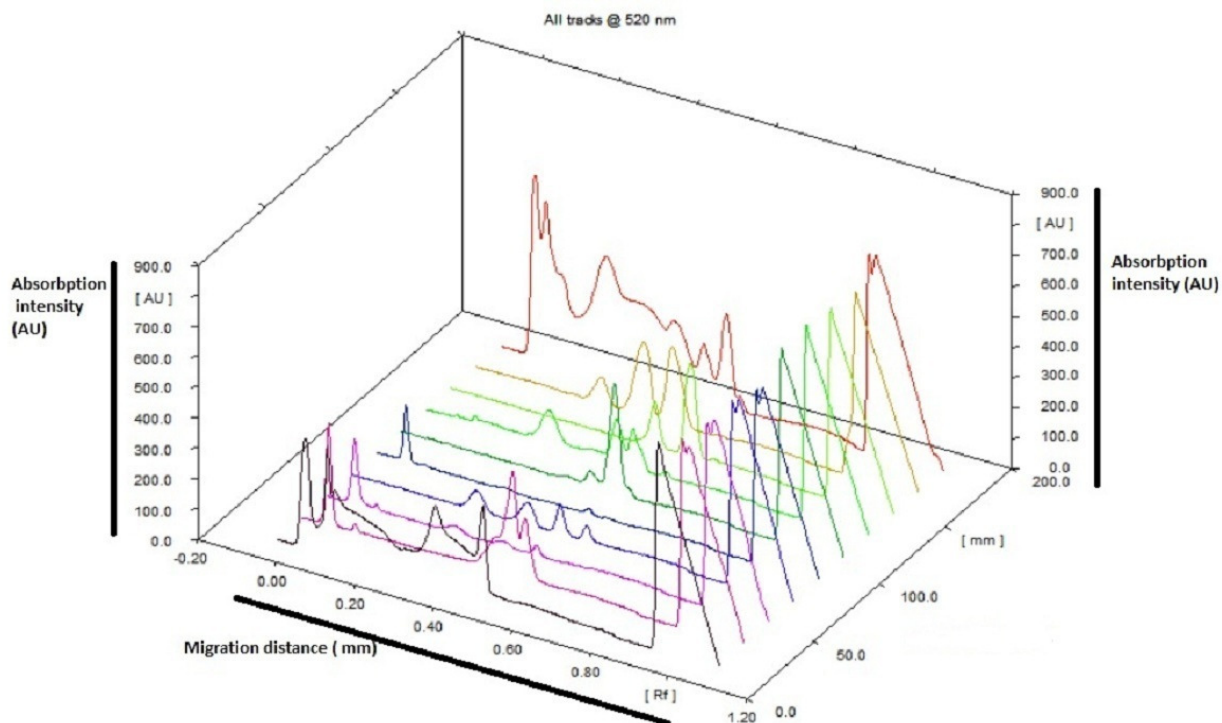


Figure-1

HPTLC 3D spectra of sample number 1-10 (extracted with Ethanol) with Solvent System I

Results and Discussion

Picric acid (as control) has been spotted along with the extracted samples and the hR_f value recorded was 90 in both solvents I and II.

In solvent system I, twenty (20) samples (extracted with picric acid and ethanol) were completely differentiated (figure-2 to 3).

Twenty (20) samples, extracted with picric acid were completely differentiated from each other in solvent system I. Picric acid (as control) have also been spotted along with the samples and the hR_f value recorded was 90 for both solvents. In solvent system I all samples (extracted with ethanol) were completely differentiated from each other.

In solvent system II, twenty (20) samples (extracted with ethanol) were differentiated into 14 groups, on the basis of differences in the number, color and hR_f value of spots (table-3). Remaining six samples were put into three different groups on the basis of similar number, color and hR_f value of spots. This might be because of two reasons. First, the same type of dye might have been used by various manufacturers during ink formulation. Secondly, the inkjet ink might have been manufactured in bulk by one company and distributed under different brand names.

Analysis by High performance thin layer chromatography (HPTLC): In HPTLC analysis, two solvent systems [I and II]

were used for the analysis of colored inkjet inks. Extracted samples were sprayed in the form of bands by automatic TLC sampler. The results were interpreted on the basis of differences in number, color and hR_f value of spots under visible and UV light (short and long wave). For better separation and resolution, HPTLC plates were scanned under TLC SCANNER 3 in absorption visible mode at 520 nm. As a result, more spots were detected. For example, in sample 1 (table 4), no spot was observed under visible light but when the same plate was scanned at 520 nm, four spots were observed (table-5). This is due to the high detection sensitivity of the scanner which detected even the non visible spots (present in less concentration).

In solvent system II, twenty (20) samples (extracted with picric acid) were differentiated into 16 groups on the basis of differences in the number, color and hR_f value of spots (figure-2 to 3). Remaining four samples were put into one group as they did not show any spot. When the same plates were scanned at 520 nm, more spots were detected. This led to further differentiation of ink samples into 19 groups. Remaining one sample did not show any spot.

Similarly, in solvent system II, twenty (20) samples (extracted with ethanol) were differentiated into 16 groups on the basis of differences in the number, color and hR_f value of spots (figure-4 to 5). Remaining four samples were put into one group as no spot has been observed. When the same plates were scanned at 520 nm more spots were detected. This led to further

differentiation of ink samples into 18 groups. Remaining two samples did not show any spot.

Table-3
TLC of Inkjet Printer Inks with Solvent System II (extraction of samples with Picric Acid)

Sample No.	Solvent System –II								
	Under Day Light			Under Short U.V Light			Under Long U.V Light		
	No of Spots	Color of Spots	hR _f	No of Spots	Color of Spots	hR _f	No of Spots	Color of Spots	hR _f
1	2	Pink	6	-	-	-	-	-	-
		Yellow	8						
2	3	Brown	6	1	Orange	24	1	Orange	24
		Blue	12						
		Pink	24						
3	3	Yellow	10	1	Orange	24	1	Orange	24
		Blue	16						
		Pink	24						
4	2	Blue	16	1	Orange	34	1	Orange	34
		Pink	34						
5	2	Yellow	10	1	Orange	24	1	Orange	24
		Pink	24						
6	3	Yellow	6	-	-	-	-	-	-
		Blue	12						
		Pink	20						
7	3	Brown	6	-	-	-	-	-	-
		Yellow	10						
		Yellow	46						
8	2	Yellow	10	-	-	-	-	-	-
		Pink	50						
9	3	Blue	10	1	Orange	30	1	Orange	30
		Blue	18						
		Pink	30						
10	3	Yellow	10	-	-	-	-	-	-
		Brown	40						
		Blue	60						

Temperature- 34°C

Table-4
HPTLC of Inkjet Printer Inks with Solvent System II (extraction of samples with Picric Acid)

Sample No.	Solvent System – II								
	Under Day Light			Under Short U.V Light			Under Long U.V Light		
	No of Spots	Color of Spots	hRf	No of Spots	Color of Spots	hRf	No of Spots	Color of Spots	hRf
1	-	-	-	-	-	-	-	-	-
2	1	Pink	6	1	Orange	6	1	Orange	6
3	2	Blue Pink	4 6	-	-	-	1	Orange	6
4	2	Pink Brown	6 14	1	Orange	6	1	Orange	6
5	-	-	-	-	-	-	1	Orange	6
6	1	Pink	6	-	-	-	-	-	-
7	1	Yellow	16	-	-	-	-	-	-
8	1	Pink	16	-	-	-	1	Orange	16
9	1	Pink	4	1	Orange	4	1	Orange	4
10	1	Brown	12	-	-	-	1	Violet	12

Temperature- 34°C

Table-5
HPTLC of Inkjet Printer Inks with Solvent System II (extraction of samples with Picric Acid) at 520 nm

Sample No.	No. of spots	hR _f Value
1	4	4, 42, 53, 78
2	5	3, 8, 4, 78, 86
3	4	3, 41, 78, 86
4	4	4, 14, 81, 86
5	3	4, 8, 86
6	2	4, 7
7	1	4
8	2	4, 14
9	2	4, 7
10	3	4, 11, 84

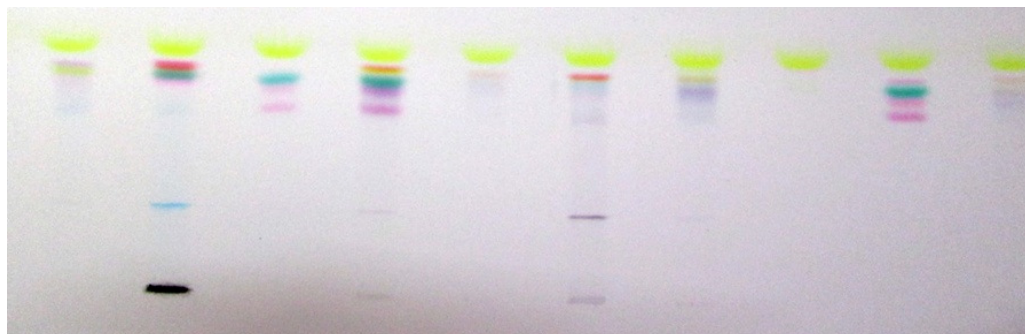


Figure-2

HPTLC Chromatogram of Sample number 1- 10 (extracted with Picric Acid) under Daylight (Solvent System I)

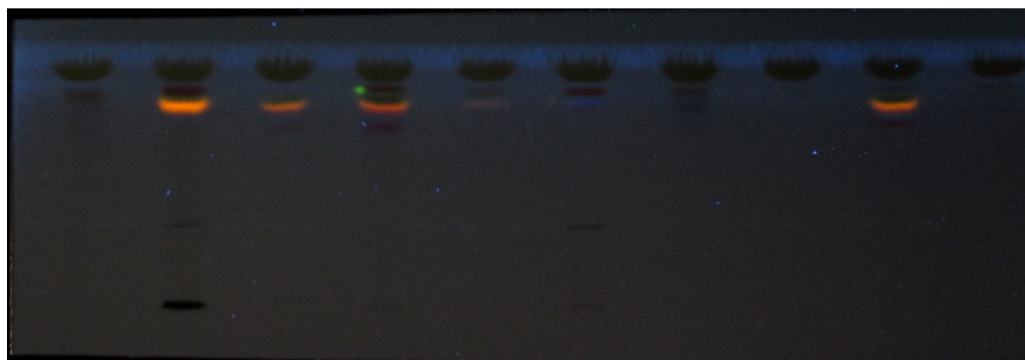


Figure-3

HPTLC Chromatogram of Sample number 1- 10 (extracted with Picric acid) under long UV (Solvent System I)

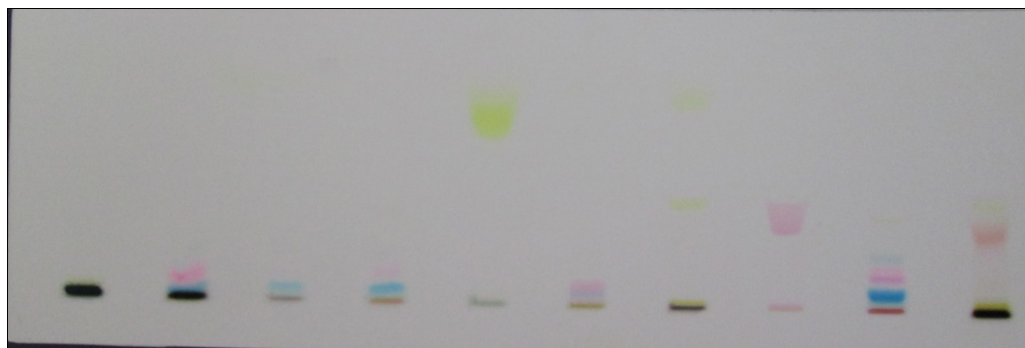


Figure-4

HPTLC Chromatogram of Sample number 1- 10 (extracted with Ethanol) under daylight (Solvent System II)



Figure-5

HPTLC Chromatogram of Sample number 1- 10 (extracted with Ethanol) under long UV (Solvent System II)

Earlier workers differentiated ball point pens inks into minor groups by HPTLC whereas when the same technique was used to study inkjet inks, major groups were discriminated. HPTLC maintains a database of inks which help in the direct comparison and identification of suspected ink with the reference ink samples. Therefore, it is suggested to maintain and develop a database of inkjet inks manufactured in INDIA.

Conclusion

Twenty colored samples of inkjet inks (both original and refilled) were analyzed by using thin layer chromatography (TLC) and high performance thin layer chromatography (HPTLC). Ink samples were extracted using ethanol. However, some of the samples were not properly extracted with ethanol. Picric acid was found efficient to extract all the ink samples. So, all twenty inkjet samples were extracted separately with ethanol as well as picric acid. Five solvent systems were tried and two solvent systems *Ethyl acetate: Ethanol: Distilled (70:35:30)* and *n-Butanol: Ethanol: Distilled water (90:15:10)* were found most suitable to separate all dye components present in the inkjet inks.

When an inkjet printed document is observed microscopically, it appears as a series of mixed colored dots. During an inkjet printing mechanism, all four colors print a picture in layers. Thus, the sample could be considered as a mixture and analyzed. It might happen that a document printed with multiple colors, (cyan, magenta, yellow and black) does not appear in equal intensity. However, intensity of colors does not affect the results; the difference appears only in the intensity of spots. So, it is possible to distinguish ink cartridges more efficiently by HPTLC.

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