

Analysis of Different Ball Point Pen Inks using thin layer Chromatography

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ABSTRACT

The present study focuses on the classification and preliminary identification of black, blue, and red ballpoint pen inks using thin-layer chromatography (TLC). Normal-phase TLC was employed to separate the dye components present in different ink samples. The inks were classified into two distinct groups based on their retention factors (Rf). A clear separation of dyestuff bands with distinct color tones was observed, enabling effective differentiation among the ink samples. The variation in the Rf values and color patterns provided a reliable basis for grouping inks with similar chemical compositions. The results demonstrate that TLC is a simple, rapid, and cost-effective analytical technique for the preliminary examination and identification of ballpoint-pen inks. This method is particularly useful in forensic document analysis for detecting and investigating document forgery cases.

Keywords:- Forensic analysis, Ball pen ink, TLC

1. INTRODUCTION

Ink analysis is an important aspect of forensic work. It can tell us a lot about a document that we are unsure about. The ink we use today has many components that improve its quality. The coloring material is an important part of the ink. The material can be either a dye or a pigment. This can be a mixture of both. Dyes can dissolve in the ink. We also refer to this part as a vehicle. On the other hand, pigments are extremely fine powders. They are composed of molecules and do not dissolve in the vehicle. Ink analysis and the study of ink are very important in this field. Modern inks and their characteristics make ink analysis useful. The vehicle in ink is important because it affects the flow and drying of the ink. The vehicle is composed of oils, solvents, and resins. Other components, such as driers, plasticizers, waxes, greases, soaps, and detergents, are used to obtain the desired characteristics of the ink. There are two techniques for analyzing inks: non-destructive and destructive approaches; the non-destructive method is better because it does not damage the ink. There are not as many nondestructive techniques available for forensic examiners. The method that works well is using IR absorption and luminescence in a special machine, such as a video spectral comparator. This is especially beneficial for inks. There are ways to do this without damaging the ink, such as Raman and surface-enhanced resonance Raman spectroscopy and UV-Vis micro-spectrophotometry. If you take a piece of the ink line and use a solvent to extract the ink, then you can perform even more tests on the ink. Methods such as thin-layer chromatography, high-performance liquid chromatography, infrared spectroscopy, and capillary electrophoresis are used to examine inks. Thin-layer chromatography is widely used because it is fast, inexpensive, and does not damage documents. When this method is used, the chromatograms are often examined. The retention factor values are used to obtain an idea of what we are looking at. This is not a very accurate way to do things, especially when we want to compare the ink to a large collection of chromatograms that we already have. We must use layer chromatography and other methods, such as high-performance liquid chromatography, to understand the composition of the inks. Direct scanning of chromatograms can be performed using scanning densitometers; however, it has a low signal-to-noise ratio because of the large scanning area arranged initially as the diameter of the largest spot.

In the present paper, we have described a preliminary preparation of standard TLC library for ink, also discusses the effectiveness of TLC for identification of writing implements

2. MATERIALS AND METHODS

Table 1: 9 ball point pens were purchased from local market the trademarks of collected samples are listed in Table 1

Sr. No.	Name of Ball Point Ink Pens	Code
1	Reynold Brite Blue	Reynold Blue
2	Reynold Brite Red	Reynold Red
3	Reynold Brite black	Reynold black
4	Cello Brite blue	Cello blue
5	Cello Brite Red	Cello Red
6	Cello Brite black	Cello black
7	Cello Griper Blue	Cg blue
8	Cello Griper Red	Cg red
9	Cello Griper Black	Cg black

3. TLC ANALYSIS

A developing chamber was prepared by adding approximately 5 mL of developing solution to the chamber (Figure 1). Appropriate sections were removed from the specimen document with a pair of scissors, cut into a few pieces, and placed in a 10 × 75 mm test tube. If variations in ink on one document were suspected, different sections were separated and labeled. The ink was extracted from the paper using 2-3 mL of methanol. The test tubes were heated in a water bath to increase ink solubility. To remove the ink from the paper pieces, hot methanol was squirted over the paper pieces using a Pasteur pipette. When the methanol solution was fairly dark from the ink, the ink solution was transferred from the test tubes to a small tube.

Spotting of Sample

The TLC plate was handled only by the edges, ensuring that the white silica layer was not touched. A pencil and ruler were used to draw a line approximately 1 cm from the bottom of the plate. A capillary tube was immersed in the sample tube until some of the liquid was drawn into the capillary. The small end of the capillary tube was gently pressed at the crosshair on the TLC plate. A small spot was created by quickly touching the capillary to the plate and then removing it immediately. The spot was allowed to dry, and spotting was repeated directly over the original spot. A UV lamp was used to visualize the spots.

Three different developing solvents were used for the analyses.

Developing Solvent 1: *n*-butyl alcohol: ethyl alcohol: water: acetic acid - 60: 10: 20: 0.5

Developing Solvent 2: methanol: acetone: water- 40: 40: 19.5

Developing Solvent 3: acetic acid: pyridine: methanol- 40: 40: 19.5



Figure 1: Spots of different inks on TLC plates in solvent 1

The position of the sample spots on the thin-layer plate and the solvent level in the chromatography jar were carefully checked. The plate was placed vertically in the developing jar with the upper edges resting against the jar. The jar was resealed, and the solvent was allowed to rise until it was approximately 2-3 cm from the top of the plate. The TLC plate was removed using tweezers and immediately marked where the solvent stopped rising with a pencil. This is known as the solvent front. The TLC plates were then allowed to dry. The spots were visualized under UV illumination. The center of each spot was circled with a pencil, and the distance traveled by each component was measured (Fig2-7).

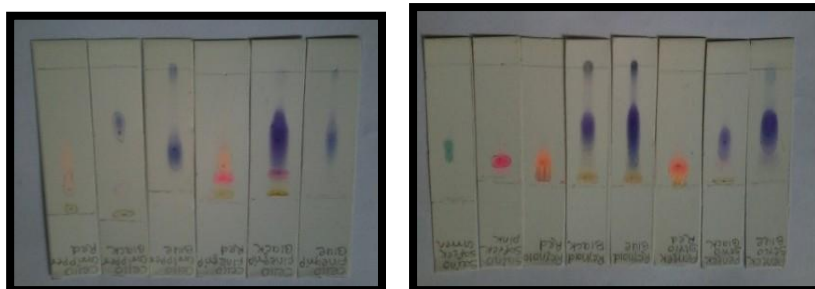


Figure 2. Spots of different inks on TLC plates in solvent 2

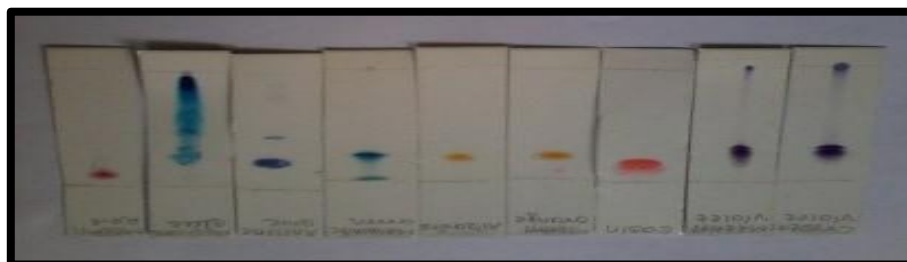


Figure 5. Spots of different standard inks on TLC plates in solvent 1



Figure 6. Spots of different standard inks on TLC plates in solvent 2



Figure 7. Spots of different standard inks on TLC plates in solvent 3

4. RESULT AND DISCUSSION

TLC: The Rf values for each sample were measured, and the results are shown in Table 2. Moreover, optimization study was done with some standard dyes given in Table 3

Table 2. TLC analysis for ink Samples

Sr. No.	No. Ink Samples	Solvent 1		Solvent 2		Solvent 3		
		Code	Colour	Rf	Colour	Rf	Colour	Rf
1	Reynold Blue		Blue	0.75	Violet	0.54	Violet	0.88
			Violet	0.74	Yellow	0.93		
2	Reynold Red		Pink	0.74	Orange	0.82	Orange	0.95
3	Reynold Black		Yellow	0.86	Violet	0.55	Violet	0.88
			Orange	0.86	Yellow	0.93		
4	Cello blue		Violet	0.78	Violet	0.53	Violet	0.84

5	Cello Red	Orange Violet	0.82 0.77	Orange Pink Yellow	0.74 0.82	Orange	0.90
6	Cello Black	Violet Yellow	0.72 0.84	Orange Pink Yellow	0.53 0.78	Violet	0.88
7	Cg blue	Violet	0.75	Violet	0.66	Violet	0.89
8	Cg red	Violet	0.71	Orange Yellow	0.83 0.96	Orange	0.95
9	Cg black	Yellow Orange	0.86 0.81	Blue Pink Yellow	0.43 0.77 0.94	Violet	0.88

Table 3 .TLC analysis Dyes

Sr. No.	Dyes	Solvent 1		Solvent 2		Solvent 3	
		Colour	Rf	Colour	Rf	Colour	Rf
1	Crystal Violet	violet	0.77	violet	0.59	violet	0.82
2	Methyl Violet	violet	0.76	violet	0.60	violet	0.80
3	Eosin	orange	0.86	orange	0.87	orange	0.92
4	Methyl Orange	yellow	0.82	yellow	0.97	yellow	0.88
5	Alizarin	yellow	0.80	yellow	0.93	yellow	0.86
6	Malachite Green	green	0.77	green	0.60	green	0.80
7	Aniline Blue	blue	0.77	blue	0.48	blue	0.80
8	Methylene Blue	blue	0.75	blue	0.45	blue	0.72
9	Methyl Red	red	0.90	red	0.93	red	0.93

Optimization study of solvents for TLC

Solvent system 1

n-Butyl alcohol/ethyl alcohol/distilled water/acetic acid (60:10:20:0.5): This solvent system showed better separation; however, it was not very good because it did not separate some of the components. Very little separation was observed, so the dyes appeared to come together.

Solvent System 2: Methanol/acetone/distilled water (40:40:19.5): This solvent system showed much clearer separation than the other solvents. Moreover, clear spots appeared, and the components were clearly separated.

Solvent System 3 Acetic acid/pyridine/methanol(40:40:19.5): There was some trailing. Separation was not as good as in other solvent systems because of trailing dyes.

The results were affected by the selection of the proper extraction solvent to remove the ink from the plate. Methanol has been reported as a solvent used with ballpoint pen inks. In this study, extraction was performed using different solvents. The obtained results revealed that immersion of paper into methanol and simple agitation could result in complete extraction of inks from paper. Methanol was selected based on its safety. The choice of the plate (stationary phase) and mobile phase was made based on the nature of the sample. Many types of TLC plates were examined, and it was found that silica gel plates provided better resolution of dye spots. Alumina sheet silica gel was preferred in these studies because of its ease of handling. Many mobile phase system were investigated in this work then few mobile phase were selected and found that solvent system-2 methanol/acetone/distilled water (40:40:19.5), was effective in separating nearly all dye mixtures

5. CONCLUSION

The results of TLC showed that blue inks 1, 4 and 7, (Inks) have a similar composition, while blue inks 1, 4, and 7 and 8(standard dyes) are different from each other. Black inks 2, 5, and 8 have two similar compositions. Similarly, red inks 3 and 9 have two similar compositions, while red inks 6 and 12 have one similar composition. Therefore, therefore still has a very important role to play in the routine examination of inks, although a great deal of research is currently underway involving the evaluation of more sophisticated and sensitive instrumentation for ink analysis. Our results and final conclusion suggest that the TLC technique is complementary and very useful.

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