PROJECT REPORT

On

A Comparative Study on Pen Inks Through Thin Layer Chromatography and Gas Chromatography

Submitted in Partial Fulfilment of the Requirement for

the Degree of M.Sc. Forensic Science

Submitted by

Rishabh Gupta

M.Sc. Forensic Science (IV Semester)

Under the Supervision of

DR. MAMTA



Division of Forensic Science School of Basic and Applied Science GALGOTIAS UNIVERSITY Uttar Pradesh

CERTIFICATE

This is to Certify that Mr. **RISHABH GUPTA** has carried out his project work entitled "A COMPARATIVE STUDY ON PEN INKS THROUGH THIN LAYER CHROMATOGRAPHY AND GAS CHROMATOGRAPHY" under the supervision of **Dr. MAMTA** (GUIDE). This work is fit for submission for the award of Master Degree in Forensic Science.

Dr. Lalit pratap chandravanshi Division chair Division of forensic science (SBAS)Galgotias university Dr. Mamta (supervisor) Associate professor Division of forensic science (SBAS), Galgotias university

Dr. AK JAIN

Dean School of Basic & Applied Sciences (Galgotias University)

CANDIDATE DECLARATION

I hereby declare that the dissertation entitled "A COMPARATIVE STUDY ON PEN INKS THROUGH THIN LAYER CHROMATOGRAPHY AND GAS CHROMATOGRAPHY" submitted by me in partial fulfillment for the degree of M.Sc. in Forensic Science to the Division of Forensic Science, School of Basic and Applied Science, Galgotias University, Greater Noida, Uttar Pradesh, India is my original work. It has not been submitted in part or full to this University of any other Universities for the award of diploma or degree.

RISHABH GUPTA

ENROLLMENT NO. 18022010034

M.Sc. Forensic Science (IV Semester) Division of Forensic Science School of Basic and Applied Science Galgotias University Greater Noida Uttar Pradesh, India

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PROJECT SUMMARY

Ink analysis is helpful in forensic science for the lithographic paper or other surfaces in which remains of inks are commonly used and reliable for corporate and legal work. Forgery of a questioned document is a common crime and of great importance in forensic science. Objectives are a collection of different pen and printing ink and different grade of documents for analysis, analysis of the inks; documents collected by Thin Layer Chromatography, optimization of the solvent system for precise and accurate analysis of the type of pigment present in the inks and to study and identify the solvents used for manufacturing different pen inks by gas chromatography using headspace extraction technique and Thin Layer Chromatography. This research article aims to show the importance of Thin Layer Chromatography and Gas Chromatography in the forensic analysis of inks of all sorts of pen. Ink analysis is very useful in forensic examination. In this research work, among those 26 ink samples, 19 were of ball point pen ink including red, black, green and blue color. 4 ink sample were of pilot pen ink and 3 ink samples of fountain pen ink used as a sample in this research work. All these ink sample has been collected and examined with the help of Thin Layer Chromatography.

Keywords: Thin Layer Chromatography, Ink analysis, Gas Chromatography, etc.

INTRODUCTION

Document examination has always been an important part of forensic examination. Different analytical techniques are used in order to decipher the activities such as disguise, forgery, etc. used in a document for the purpose of deception. Researches have been done to determine the characteristics of inks so that the age and difference of inks can be determined using the composition of inks such as resins, solvents, dyes, etc. Manufacturers of Inks use different combination to make a better quality of inks and in a process many different inks have been established till now making it difficult for the forensic document examiners to analyse an ink due to different and secret composition of different brands of inks.

With the increase in the crimes related to documents examination of the questioned document becomes necessary and to prove the authenticity of a questioned document ink analysis play an important role.

Though all the inks may look alike but there are some differences in their composition which can be revealed with ink examination and result may help in determining any alteration to a document, forgery, etc. [3] A document involves numerous elements such as paper, ink, stamps, etc. Documents are written in huge numbers with the writing inks which has led to several crimes related to a document and therefore, investigation of a document has become necessary. [10]

The technique Thin Layer Chromatography (TLC) is used for separating the components of ink on a stationary phase with the use of the mobile phase. Inks used whether printing, stamping or writing ink consists of different components and TLC is used to separate them. TLC is used broadly all over the world or ink analysis due to its reasonable equipment compared to other techniques and requires less training. [4] Ink analysis is an important procedure for revealing important information about the document. Modern inks contain different components to make much more characteristic.

Among all the ink components colour is the most important material which comes in the form of dyes, pigments or their combinations. Ink consists of pigments, dyes, resins, solvents, etc.

to colour the surface, create a design, text or an image. Inks in liquid form are usually used in writing pens while thicker inks in paste form are extensively used in printing inks. Ink can be a complex medium composing of solvents, pigments, dyes, resins, lubricants, surfactants, particulate matter, fluorescents and many other substances. Components of ink serve different purposes such as; ink's carrier, colorants, additives affecting the flow and thickness of the ink and its dry appearance. Samples of ink in the pen can be applied directly to the TLC plate while the ink in a cloth needs to be removed at first using the solvent and then is applied to a TLC plate. The solvent is taken in a heating tube for at least one hour and then solvent can be spotted on a TLC plate.

When the ink sample needs to be taken from a paper, the same procedure needs to be followed except the heating of sample as well as solvent. We need to cut off the section of the paper which includes the ink, then place it in a tube consisting of a solvent until the ink is dissolved. After the ink is dissolved in the solvent, it can be used for spotting onto a TLC plate.

After the spotting, TLC plate is run where different bands are visible on the plate which indicates separation of ink components. Colour bands and Rf values of the samples are recorded and can be compared with the database of inks. This comparison will help in the identification of the ink used and it is possible that the specific pen matches the ink in a particular database of inks. As the manufacturing companies of the ink add different components in the inks to add new features the comparison differs and make it difficult.

In situation where a writing needs to be identified whether written by the same pen, both samples needed to be run on the TLC plate and then directly compare the differences between them. During this the conclusions must be made effectively. The matching of the bands may mean that the note was written by the same pen and vice-versa. As there are many inks that contain the same ink, we cannot conclude that the pen was written by the specific pen based on one particular test. However, if the result is combined with other tests which suggest the same result, the conclusion will become easy if the note was written using same ink.

Since, there is not a large database of band patterns available, TLC is mostly used for comparison of two specific samples of inks instead of identifying the sample from the unknown sample. It is also possible that different fibres are used in same inks which doesn't make it a strong case to use this as evidence to conclude a result. However, this may be used to support the conclusion.

OBJECTIVES

- 1. Analysis of the inks & documents collected by Thin Layer Chromatography.
- 2. Optimization of the solvent system for precise and accurate analysis of the type of pigment present in the inks.
- 3. Study and identify the solvents used for manufacturing different pen inks by gas chromatography using headspace extraction technique.

REVIEW OF LITERATURE

Komal Saini, (2018) suggested the gel-pen ink differentiation using HPTLC (High performance Thin-Layer Chromatography) and GC-MS (Gas Chromatography-Mass Spectrometry), chromatography and gas chromatography-mass spectrometry, in gel pen ink few components are volatile. According to this study, the author has collected 90 gel pen inks from the stationary shops in India. Each of the pen was used to write" PASSPORT' on the white A4 sheet, every paper was stored in a separate envelope.

In this study 60µl ethanol was used for the examination, 28 gel-pen inks were examined by (HPTLC) High Performance Thin Layer Chromatography and 62 gel pen inks were examined by gas chromatography. The result of this study is both of the techniques were used in this study proved to be the better result compare to other techniques.

Jyoti Yadav, (2018) talked about the characterization of ballpoint pen ink by using nondestructive methods. Document forgery is common as the illiteracy is rising. Ink examination includes equally chemical and physical examinations. Video spectral comparator stood used to detect the optical stuff of inks. According to this study, the FTIR instrument remained cast-off to acquire the fingerprint spectra of ink of dissimilar brands. It is not possible to make a pure discriminate among all varieties of pen inks, in this study only 2 pen inks visible out of 10 pen inks.

Kiran Yadav, (2017) talked about the forensic importance of ink analysis based on planar chromatography. In this study author was collected 10 pens of different colors from the market of Delhi/NCR, administrated work was carried out on inks extracted from the ink entries made on white duplicator paper. All the pens were used to write "BLAST" on the plain paper and then analysis based on solubility test, paper chromatography and thin-layer chromatography. In both of the techniques the extraction chemical is methanol. In this study the blue pen ink was found to non-polar solvents whereas soluble in polar solvents. The separation of the ink in thin layer chromatography was good and spots were detected while in paper chromatography is a much better examination technique of ink analysis.

Loong Chuen Lee, (2016) talked about the red pen ink analysis based on ultra-performance liquid chromatography (UPLC), ultra-performance liquid chromatography is more active than other chromatographic techniques. In this study author was collected 12 red pens to be studied. Four different individual pen samples are used for the extraction by ultra-performance liquid chromatography, the four samples were used to write "INDIA" three times on a plain white sheet. Examination based on the ACQUITY UPLC system; an examination was performed by water. The ink was inserted on the AQUITY UPLC column the particle size of 1.8mm was used to separate the ink sample. This study means to analyze the chance of discriminating red pen inks explanation info obtained from parts apart from dyes.

Dr. Joseph Sherma (2016) talked about developments in the ink analysis by thin-layer chromatography and high-performance thin-layer chromatography. In this study the ink sample was directly applied to the stationary phase, and make running solvent by water, ethanol, butanol, etc. 20µl ink sample was injected on silica gel glass plate and run on the covered container.

HPTLC plates having thinner layers relate to TLC plates, HPTLC can give advanced resolution and quicker separation. Ink samples were clearly separated by both of the techniques.

M. Irfan Nunkoo, (**2016**) talked about the examination of red, black, blue and green pen inks. In this study total of 78 ink samples were collected (24 black, 21 blue, 18 red and 15 green) and purchased from the retail market of Mauritius. According to author 5 different methods used in this study of examination of ink (thin layer chromatography, Raman spectroscopy, filtered light examination, Fourier transform infrared and visual spectroscopy). In this study using 5 different techniques TLC, FTIR, FLI, VIS and RAMAN SPECTROSCOPY. By all these techniques ballpoint pen inks could be magnificently separated.

Alicja Menzyk, (2016) talked about the physicochemical analysis of ink – dating and establishing the sequence of intersecting lines of ink entries. Nowadays Ink dating is a tremendously interesting matter, it is the most important task that forensic experts face, in this study the author was using the static dating method. Approaches to ink dating, static approach and dynamic approach. According to the author in this study the method of ink dating is not reliable.

Sharma N, (2014) talked about the analysis of black pen inks. Two black pens of different brands were used to analyze this study, the methods used in this article is TLC and NMR. Separate color bands are visible by TLC and compare by rf value of the ink. NMR analysis is not easy to separate these inks.

Roger W. Jones, (2013) talked about writing inks on paper through real-time mass spectrometry (DART-MS), according to this study authors were directly ink applied on real-time mass spectrometry of gel pen ink. In this study the mass spectra remain easily found since ink on paper destitute of visual alteration of the document.

Stephanie Houlgrave, (2011) in his journal talked about writing inks analyzed using thin-layer chromatography. In this study author was collected 29 ink samples including 21 (5 black and 16 blue, by 7 different manufacturers) distinct ink preparation was designated for analysis. Extraction chemical is methanol, ethanol, butanol and ethyl acetate, the extracted ink samples were injected on silica gel plate with a layer of thickness 250µm, micropipettes were used to transfer extracted ink samples on the silica gel glass plate. Total no. of ink samples was analyzed using thin-layer chromatography, in this learning also using ambient transmitted light to evaluate the chromatographic contours.

Djozan, (2008) suggested ink differentiation of questioned documents by coming up with an image analysis software system. The ink spot is extracted from documents victimization wood spirit and separated on colloid sixty plastic sheets by horizontal development with alkyl radical acetate-ethanol-water mobile part. a replacement software system program. Discriminated chromatograms of various inks imaged by a standard workplace scanner based on intensity contours of red, green, and blue inks. DP of the method was ninety-two.8% among completely different pen inks, and blue ballpoint inks of forty-one completely different samples from the native market were with success analyzed and discriminated.

V. S. Hatzistavros, (2008) talked about ink spiking for signature authentication, commercial ink was used in this examination of ink, this ink was placed in a glass tube and two inks were created by a metallic substance in the sample tube. The production of labeled ink with inorganic and organic elemental constituents provided a brand-new kind of ink that may be vital on the practicableness of victimization the above technique in rhetorical sciences and specifically in cases of safety features, fraud and counterfeiting.

Craig D. Adam, (2008) talked about individualization of black ballpoint pen inks using principal component analysis of UV–vis absorption spectra, the analysis is to regulate whether two pieces of written text initiated from the same pen. In this study 25 black ballpoints pen were collected by the author and purchased from the UK market. The examination method in this learning is Principal component analysis and Thin layer chromatography. PCA to differentiate between black ballpoint pen inks and to examine the measurable changeability among the same brand of pen. As TLC is a static technique for the forensic examination of ballpoint pen inks, a chromatogram for each of the inks and the detached ink lines, detected in this work, was similarly produced.

Valerio Causin, (2008) talked about the examination of black and blue ballpoint ink through thin layer chromatography, ultraviolet-visible spectrophotometry and Fourier transform infrared spectroscopy. Total no. of ballpoint inks was collected by the author is 33 (different manufacturers, 21 black and 12 blue) purchased from stationery shops in the region of Messina. FT-IR technique is commonly used for the examination of non-colorant components in writing inks. No differences detected between 2 samples, and the other 31 samples were separated by UV spectrophotometry, TLC and FTIR.

Hu-Sheng Chen, (2002) talked about methods used for the identification and characterization of the ink, in this study author was using 9 techniques for the examination of ink identification (thin layer chromatography, high-performance liquid chromatography, capillary electrophoresis, laser excitation and spectroscopy, diffuse reflectance Fourier transform infrared, luminescence photography, paper chromatography and paper electrophoresis and micro spectrometry). In this study all of the methods were successfully examined by the laboratory procedure by using different instruments.

MATERIALS AND METHODOLOGY

CHEMICALS

The chemicals used throughout the experiments were methanol, ethanol, ethyl acetate and acetone, distilled water. The TLC silica gel plate with layer thickness 0.25 mm and 20 x 20 cm aluminum cards.

SAMPLE COLLECTION

Gel pen ink, Ball pen ink and printer inks will be collected from different sites. Relative documents would also be collected for extraction of inks from the documents.

TESTING OF SAMPLES

FIG 1 (BLUE INK, DILUTION WITH ETHANOL)

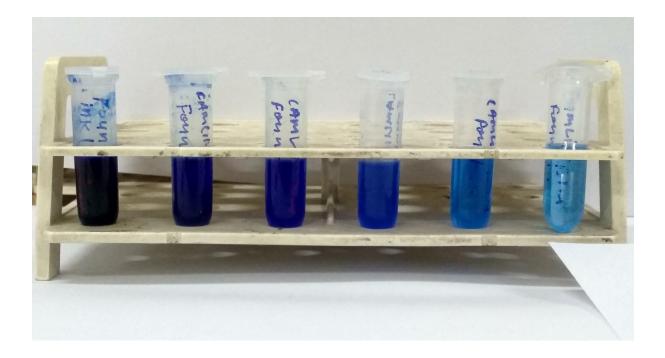


FIG 2 (GREEN INK, DILUTION WITH ETHANOL OR WATER)



FIG 3(BLACK INK, DILUTION WITH METHANOL)

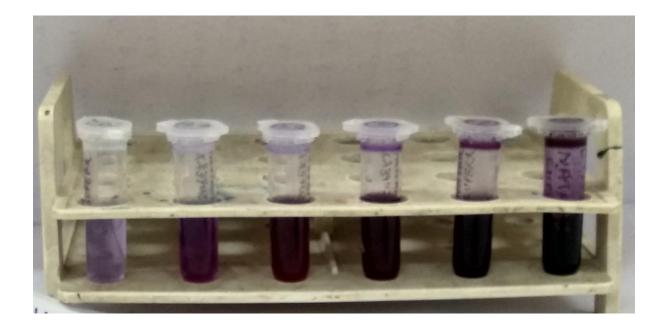
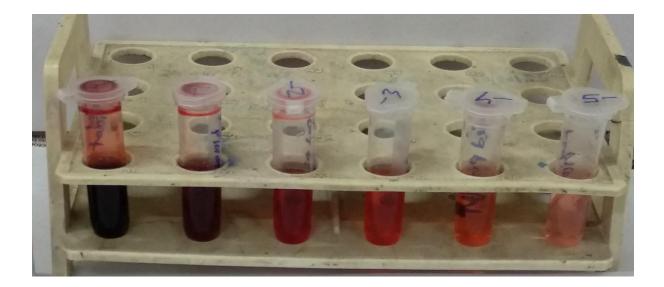


FIG 4 (RED INK, DILUTION WITH ETHANOL)



The samples then will be tested using Thin layer Chromatography (TLC) and Gas Chromatography (GC).

TYPES OF PEN INK

Ballpoint. Ink base: Oil. Pigment or Dye.
Fountain. Ink base: Water. Pigment or Dye.
Rollerball. Ink base: Water. Pigment or Dye.
Gel. Ink base: Water. Pigment or Dye.
Drawing (Dip Pen) Ink base: Pigment or Dye.

SOLVENT USED FOR THE EXTRACTION

Ethyl acetate, Ethanol, Acetic acid, Acetone, Butanol, Tetrachloroethane, Cyclohexane, Methanol (soluble), Pyridine (soluble)

Thin Layer Chromatography of INK samples:

The ink mixed with the solvent was examined on the TLC plate to calculate the retention factor (rf) value of the different ink forming pigments. Following procedure was used for examination:

Step 1: Preparation of TLC plate:

i. Three clean glass slides were taken.

ii. In a beaker thin slurry was prepared by adding 3gm of silica powder and 6ml water.

iii. Slurry was poured onto glass slides and dried at room temperature. Glass slides were kept in a hot air oven at 55° for 15-20min, for activation of TLC plates.

Step 2: Preparation of solvent:

1. Different Solvents were prepared (Ethanol+Water, Methanol+Water, Ethanol+Methanol+Butanol+Water).

Step 3: Loading of TLC plates

- 1. With the help of a tip, point was marked and 10-15µl (microliter) ink solution was loaded.
- 2. Vertically glass plates were placed into solvents and covered with a lid.

Step 4: Visualization/Detection of TLC plates:

1. After completion of running, the TLC plates were dried and examined for bands.

Step5: Calculation of retention factor (rf) value:

Rf value was calculated by measuring the distance travelled by solute and solvent on a chromatographic plate.

The components of the inks are separated with the help of the solvent, because of different affinity of solutes for mobile phase on a Silica gel. They are pulled up with the help of the solvent. The solutes with high affinity towards the solvent will move further up than the low affinity solutes. Solutes will be seen close to the starting point if they spend more time on stationary phase. The dye separation pattern is different than the ink separation pattern which consists of different dyes providing many different points for the comparison between a questioned and a known ink sample.

As the solvent reaches towards the end point of the TLC plate, the plate is removed from the TLC chamber and is dried. Position of different components are marked and then the Rf value is calculated.

 $Rf = \frac{The}{distance} \frac{traveled}{traveled} \frac{by}{the} \frac{the}{solute}$

RESULTS AND DISCUSSION

The present investigation was undertaken to analyse the INK pigments through Thin Layer chromatography and Gas chromatography. The Pen ink is matched with the questioned documents to analyse its forensic aspects.

Initially different types of Ink containing Pens were purchased and then the solvent was determined to solubilize the inks.

S.NO	TYPE OF INK	MANUFACTURER	COLOR OF	
		OF INK	INK	
1	BALL PEN INK	REYNOLDS	BLUE	
2	BALL PEN INK	GOLDEX	RED	
3	BALL PEN INK	REYNOLDS	GREEN	
4	BALL PEN INK	FLIX	BLACK	
5	BALL PEN INK	FLAIR	BLUE	
6	BALL PEN INK	CELLO	BLUE	
7	BALL PEN INK	ELKOS	GREEN	
8	BALL PEN INK	FLAIR	RED	
9	BALL PEN INK	CELLO	BLUE	
10	BALL PEN INK	CELLO	BLACK	
11	BALL PEN INK	CELLO	BLUE	
12	BALL PEN INK	CELLO	BLUE	
13	BALL PEN INK	GOLDEX	RED	
14	BALL PEN INK	CELLO	BLACK	
15	BALL PEN INK	CELLO	BLACK	
16	BALL PEN INK	CELLO	BLUE	
17	BALL PEN INK	CELLO	BLACK	
18	BALL PEN INK	NATRAJ	BLACK	
19	BALL PEN INK	FLAIR	BLUE	
20	FOUNTAIN PEN INK	CAMLIN	SCARLET RED	
21	FOUNTAIN PEN INK	CAMLIN	ROYAL BLUE	
22	FOUNTAIN PEN INK	CAMLIN	PERMANENT BLACK	
23	PILOT PEN INK	LUXOR	BLACK	
24	PILOT PEN INK	LUXOR	BLUE	
25	PILOT PEN INK	LUXOR	RED	
26	PILOT PEN INK	LUXOR	GREEN	

Table 1: Following Is the List of Ink Samples from Different Manufacturer That Has Been Examined Via TLC

EXAMINATION OF DIFFERENT INK SAMPLES

- 1. Ball pen ink, Fountain or Pilot pen ink.
 - Different ink samples of different manufacturer and of different colour were run on TLC.
 - Ink samples were diluted with 1000µl ethanol with small amount of ink.
 - Running solvent 80% ethanol + 20% distilled water.
 - Amount of solvent inject 10 µl

FIG 1 (FLAIR WI-FI, RED)

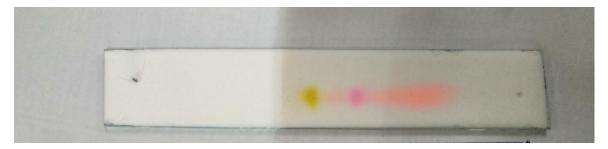


FIG 2 (CELLO MAY-FAIR, BLUE)

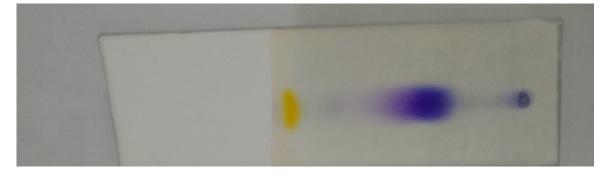


FIG 3 (CAMLIN FOUNTAIN, ROYAL BLUE)

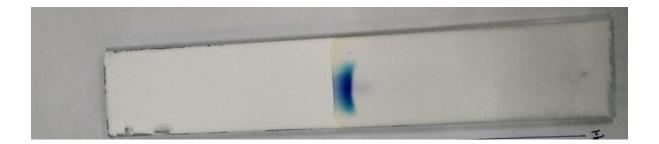


FIG 4 (CELLO TRI-MATE, BLACK)



FIG 5 (LUXOR PILOT, BLUE)

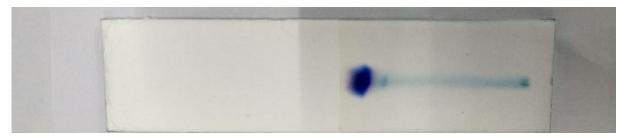


FIG 6 (ELKOSS BETTER, GREEN)

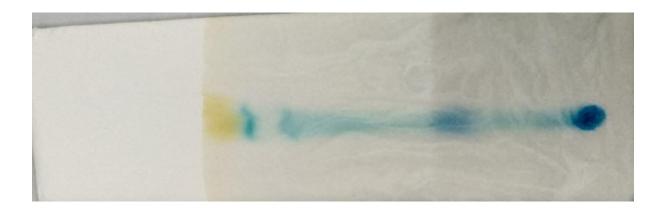


FIG 7 (CELLO ZIPPER, BLUE)

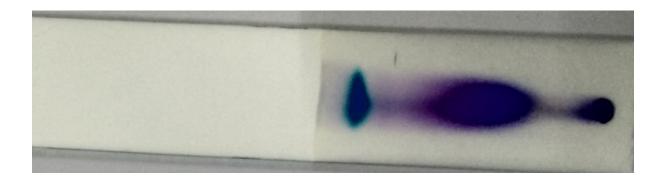


FIG 8 (GOLDEX COTTON DOLL, RED)

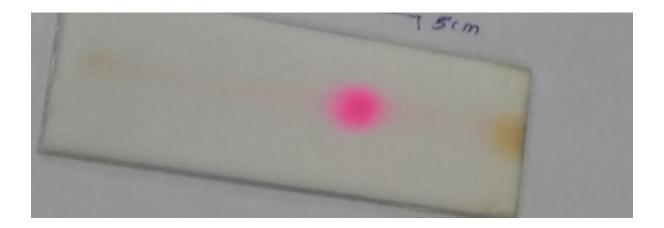


FIG 9 (CAMLIN FOUNTAIN, SCARLET RED)



FIG 10 (CELLO FAST-O, BLUE)

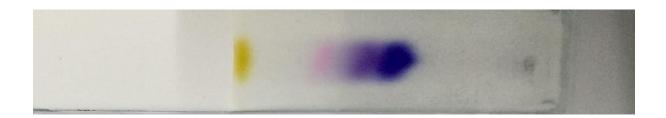


FIG 11 (CELLO NOVA, BLUE)

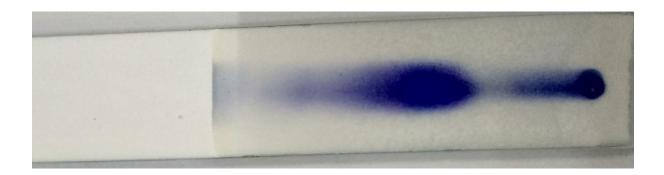


FIG 12 (CELLO FINEGRIP, BLACK)

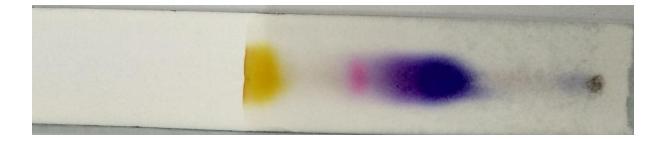
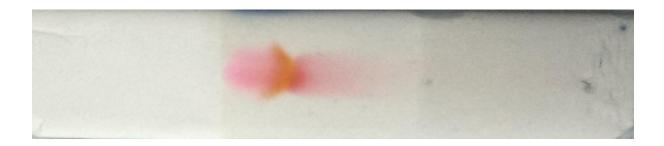


FIG 13 (REYNOLDS BRITE, GREEN)



FIG 14 (LUXOR PILOT, RED)



The following are the list of retardation factor of the ink sample analysed by thin layer chromatography (TLC). To quantify the results, the distance travelled by substance being considered is divided by total distance travelled by mobile phase. This ratio is known as retardation factor (Rf).

S.NO	INK	NO. OF	SOLVENT	RETARDATION
		SOLUTE	RUN	FACTOR
1	FLAIR WI-FI	3	10.8CM	1-1.148CM
	(RED)	1-9.4CM		2-1.402CM
		2-7.7CM		3-1.542CM
		3 – 7CM		
2	LUXOR	3	9.7CM	1-1.031CM
	PILOT (BLUE)	1-9.4CM		2-1.114CM
		2- 8.7CM		3-1.328CM
		3- 7.3CM		

3	CELLO TRI-	3	7.9CM	1-1.097CM
3	MATE	-	7.9CM	
		1-7.2CM		2-1.316CM
	(BLACK)	2-6CM		3-1.975CM
4		3- 4CM		1.00CM
4	CAMLIN	1	9.1CM	1.09CM
	FOUNTAIN	1-8.3CM		
	(ROYAL			
5	BLUE)	3		1 1.042614
5	CELLO	e	9.8CM	1 - 1.042CM
	MAYFAIR	1 - 9.4CM		2-1.324CM
	(BLACK)	2-7.4CM		3- 1.814CM
6		3- 5.4CM	OCM	1 0.975CM
6	REYNOLDS		8CM	1 - 0.875CM
	BLOSSOM	1 - 7CM		2-0.562CM
7	(BLUE)	2 - 4.5CM	5014	1 1 25014
7	GOLDEX		5CM	1 – 1.25CM
	COTTON	1-4CM		
0	DOLL (RED)	1	7.0014	1 0.000014
8	REYNOLDS	1	7.8CM	1-0.923CM
	BRITE	1 – 7.2CM		
	(GREEN)	2		1.1.101014
9	FLIX HAUSER	3	9.8CM	1-1.101CM
	(BLACK)	1 - 8.9CM		2-1.324CM
		2 - 7.4CM		3-1.606CM
10		3 -6.1CM	0. (C) 1	
10	FLAIR SNAP	e	8.6CM	1-1.162CM
	(BLACK)	1-7.4CM		2-1.178CM
		2- 7.3CM 3- 5CM		3- 1.72CM
11	CAMLIN	2	8.5CM	1- 1.214CM
11	FOUNTAIN	$\frac{2}{1-7CM}$	8.5CM	1- 1.214CM 2- 1.062CM
	(PERMANENT			2- 1.062CM
	BLACK)	2- 8CIVI		
12	· · · · · · · · · · · · · · · · · · ·	2	9.2CM	1- 1.022CM
12	LUXOR PILOT (RED)	$\frac{2}{1-9CM}$	7.2CIVI	1- 1.022CM 2- 1.135CM
		1 - 9CM 2- 8.1CM		2- 1.133CIVI
13	LUXOR	2- 0.1CM	8.4CM	1- 1.063CM
15	PILOT	$\frac{2}{1-8.1}$ CM	0.40101	2- 1.166CM
	(GREEN)	2-7.8CM		2- 1.100CW
	(ORELIV)	2- 7.0CM		
14	LUXOR	3	9.3CM	1- 1.033CM
17	PILOT	1 - 9CM	7.50111	2- 1.120CM
	(BLACK)	2- 8.3CM		3- 1.207CM
		3- 7.7CM		5 1.207 CW
15	CAMLIN	3	8.9CM	1- 1.047CM
15	FOUNTAIN	3 1 – 8.5CM	0.7011	2- 1.186CM
	(SCARLET	1 - 8.5CM 2- 7.5CM		2- 1.180CM 3- 1.648CM
	(SCARLET RED)	2- 7.3CM 3- 5.4CM		J- 1.040CIVI
		J- J.4CIVI		

16	CAMUN		0.5014	1 1 214014
16	CAMLIN	2	8.5CM	1-1.214CM
	FOUNTAIN	1-7CM		2-1.062CM
	(GREEN)	2-8CM		
17	CELLO	2	7.7CM	1-1.1CM
	ZIPPER	1 – 7CM		2- 1.201CM
	(BLUE)	2- 6.4CM		
18	ELKOS	3	10.7CM	1-1.150CM
	BETTER	1-9.3CM		2-1.320CM
	(GREEN)	2-8.1CM		3-1.377CM
		3- 4.5CM		
19	CELLO MAY	3	10.3CM	1-1.240CM
	FAIR (BLUE)	1-8.3CM		2-1.492CM
		2-6.9CM		3-1.872CM
		3- 5.5CM		
20	GOLDEX	2	8.2CM	1 – 1.223CM
	KLASSY	1-6.7CM		2-1.547CM
	(RED)	2- 5.3CM		
21	CELLO	3	8.9CM	1 – 1CM
	BLING	1 – 8.9CM		2-1.182CM
	(BLUE)	2-7.5CM		3- 1.483CM
		3- 6CM		0 11100 0111
22	CELLO FAST-	4	10CM	1 – 1.086CM
	O (BLUE)	1- 9.2CM	100101	2- 1.428CM
		2- 7CM		3- 1.923CM
		3- 5.2CM		4- 2.5CM
		4- 4CM		+ 2.501
23	CELLO	3	9.4CM	1-1.305CM
25	TRIMATE	1 – 7.2CM	7.4CIVI	2-1.540CM
	(BLUE)	2- 6.1CM		3- 1.88CM
	(DLUE)	3- 5CM		J- 1.00CIVI
24	CELLO NOVA	2	10.3CM	1 – 1.157CM
24	(BLUE)	$\frac{2}{1-8.9}$ CM	10.5C.WI	2- 1.688CM
	(BLUE)	2- 6.1CM		2-1.000CM
		2- 0.1CIVI		
25	CELLO	4	10.5CM	1 – 1.117CM
23	FINEGRIP			1 – 1.117CM 2- 1.418CM
		1 - 9.4CM		
	(BLACK)	2-7.4CM		3-1.666CM
		3- 6.3CM		4-2.1CM
26		4- 5CM		1 1 1 1 2 0 4
26	NATRAJ	3	10.9CM	1 – 1.112CM
	SUPER-X	1-9.8CM		2-1.345CM
	(BLACK)	2-8.1CM		3- 1.816CM
		3- 6CM		

The chemical composition of the ink on a specific document will verify whether the known or the questioned documents were written by the same pen ink. TLC is useful in identification of the inks. TLC is very helpful in making a colour graph of the components of inks. Commercial inks for example Ball point pen is made up of several dyes which can be separated on a TLC plate. After the ink examination for the comparison and matching is done between the inks and documents written by the particular inks, the comparison would help in identifying forgeries and document relevance found on crime scene the analysis should include a summary of results (table of ink types and corresponding Rf values), which lead you to the identification of the unknown ink source. The ink analysis would be optimized to get a precise band and easy comparison. Gas Chromatography would be used to identify the ink volatiles present in them.

FUTURE SCOPE

The information obtained add to the library of the database.

Further the change is the respective dye in the respective ink can be observed and analyze for the dating purpose. Thus, the information on relative writing age can be abtained. And, the powerful evidences for identifying the age of ballpoint pen ink is provided.

REFERENCES

- 1. Komal Saini, Rajshree Rathore, "Differentiation of gel pen inks by using High performance thin layer chromatography and Gas chromatography-Mass spectrometry" Malaysian Journal of Forensic Sciences, 2018
- 2. Jyoti Yadav, "The Characterization of ballpoint pen ink by using non-destructive methods" Research Journal of Forensic Sciences Vol. 6(6), 1-6, September (2018).
- 3. Kiran Yadav, "Analysis of commonly used blue ballpoint pen ink in India by planar chromatography" International journal of advanced research, 2017.

- Loong Chuen Lee, Seow Lay Ying, Wan Nur Syazwani Wan Mohamad Fuad, Fast and Simple Forensic Red Pen Ink Analysis Using Ultra Performance Liquid Chromatography (UPLC), Malaysian Journal of Analytical Sciences, Vol 20 No 2 (2016): 224 – 230.
- Dr. Joseph Sherma (2016): Advances in the Thin Layer Chromatographic Forensic Analysis of Inks, Journal of Liquid Chromatography & Related Technologies, DOI: 10.1080/10826076.2016.1183130.
- M. Irfan Nunkoo, M. Bilall Saib-Sunassy, Henri Li Kam Wah and Sabina Jhaumeer Laulloo, "Forensic Analysis of Black, Blue, Red, and Green Ballpoint Pen Inks" Springer International Publishing Switzerland 2016.
- Alicja Menzyk, Grzegorz Zadorai, Mieczysław Sajewiczi, "Physicochemical analysis of ink – dating and establishing the sequence of intersecting lines of ink entries" Problems of Forensic Sciences 2015.
- 8. Sharma N, Agarwal A, Negi YS, "Analysis of Black Ballpoint Pen Inks" International Journal for Pharmaceutical Research Scholars (JJPRS), 2014.
- 9. Roger W. Jones, "Analysis of Writing Inks on Paper Using Direct Analysis in Real Time Mass Spectrometry" Forensic Science International 231 (2013).
- Houlgrave, S., LaPorte, G. M., Stephens, J. C. (2011). The use of filtered light for the evaluation of writing inks analysed using Thin Layer Chromatography. Journal of Forensic Sciences, 56, 778–783.
- 11. Djozan djavanshir, "Forensic discrimination of blue ballpoint pen inks based on thin layer chromatography and image analysis", Forensic science international 179:199-205
 August 2008.
- V. S. Hatzistavros, N. G. Kallithrakas-Kontos, "Trace element ink spiking for signature authentication" Journal of Radioanalytical and Nuclear Chemistry, Vol. 277, No.2 (2008) 399–404.
- Craig D. Adam, Sarah L. Sherratt, Vladimir L. Zholobenko, "Classification and individualisation of black ballpoint pen inks using principal component analysis of UV-vis absorption spectra" Forensic Science International 174 (2008) 16–25.
- Causin, V., Calamansi, R., Marega, C., Maida, P., Schiavone, S., Marigo, A., Villari, A. (2008). The discrimination potential of ultraviolet-visible spectrophotometry thin layer chromatography, and Fourier transform infrared spectroscopy for the forensic analysis of black and blue ballpoint inks. Journal of Forensic Sciences, 53, 1468–1475.
- 15. Hu-Sheng Chen, PhD, "A survey of methods used for the identification and Characterization of inks" Forensic Science Journal, 2002