CHAPTER-I

INTRODUCTION

Writing instrument or writing implement is an object used to produce writing. Writing consists of different figures, lines and forms. Most of these items are used for painting, drawing and technical drawing, but writing instruments generally have the ordinary requirement to create a smooth, controllable line.

Another writing implement employed by a smaller population, is the stylus used by blind users in conjugation with the slate for punching out the dots in Braille.

A writing instrument having a barrel and an ink cartridge shift ably mounted in the barrel and provided at one end with a writing tip. At its end, the barrel has longitudinally extending fingers which close upon themselves and completely shield the writing tip when the cartridge is in its retracted position. We can determine the type of instrument used on documents by ink analysis.

Ink analysis is an important part of the investigation of **questioned documents**, including forged checks, wills, or altered records. Although all blue or black inks may look the same, there can be some important differences in their chemical composition. These can be revealed by laboratory analysis and the results can help to know whether there have been any additions or alterations to a document. The ink may be analysed by non-destructive or destructive testing, it depends upon whether a sample needs to be taken from the document. Non-destructive ink analysis includes micro-spectrophotometry, Raman spectroscopy. Destructive ink analysis include chromatography techniques, like thin Layer Chromatography (TLC), paper chromatography etc. The sample is placed in a test tube with a solvent that dissolves the ink. A tiny spot of the sample solution is placed onto a TLC silica G plate along with other reference sample. Then the plate was placed in a beaker containing a small amount of suitable solvent system. The spots of sample remain above the solvent level. The solvent is drawn up by the paper capillary action and the sample spots move up with it. The end result with TLC is a pattern of coloured spots, known as a chromatogram, for each ink. Different inks will have different chromatograms with different R_f values. If the sample ink has the same chromatogram and R_f as one of the reference inks, it suggests they are the same, and so identification can be made.

1.1 History of writing instruments:

Writing is one of the most important inventions of humanity. It allowed us to record our history, ideas and discoveries and spread them across the globe for all to know. As the writing developed so did writing instruments and techniques. Earliest writing tools didn't use pigment to live mark on the surface but were made to be rigid so they could engrave texts into different materials. Chinese, for instance, carved into turtle shells.

Ancient Sumerians and Babylonians used triangular **stylus** to write in soft clay tablets which would be later baked. Romans wrote in wax tablets with styluses which allowed them to erase written text. These methods, of course, had their disadvantages. Clay tablets were heavy and brittle. Wax tablets were not heat resistant. Because of that people tried to find other solutions. They appeared in the form of writing tools that use pigment of some sort. Scribes of Ancient Egypt **Reed pens** were made from a single reed straw cut and shaped into a point.

As a surface for writing with these pens was used papyrus. Reed pens didn't last long when used and were too stiff so they were replaced **Quills** are pens made from flight feathers of large birds. The hollow shaft of these feathers holds the ink which flows to the tip, which is cut into the shaft, by capillary action. Different materials were used to be written on with quills, like parchment and vellum. It is known that some of the Dead Sea Scrolls, dating back to 100 BC, were written with quills. First quills were cut into a square tip and rigid and were like that for many centuries imitating reed pens.

From the 17th century, when writing became more popular, quills were made to be more flexible and cut to a point. Some hundred years earlier, deposits of graphite were discovered in England which marked the birth of pencils which didn't use ink but a core of a solid pigment, graphite in the beginning and later mixture of powdered graphite and clay. They were at first covered in leather and later in thin wooden cylinder as we still do today. They became popular because they were easy to use, couldn't spill and could be easily erased if a mistake is made, unlike ink.

Popularity of quills lasted until 19th century when the first pens with metal nibs appeared (although there were earlier tries of metal pens but they didn't catch on).John Mitchell from Birmingham was the first to mass-produce pens with metal nibs in 1822. These had a handle and a metal point with a split that held a small amount of ink when dipped. They worked the same as quills but lasted much longer, didn't need to be sharpened and could be made to a much finer point.

Folsch received a patent in England for a pen with an ink reservoir in 1809. French Government patented a **Fountain pen** in May 1827 which was an invention of Romanian Petrache Poenaru.

Ballpoint pen was invented in 1888, by John J. Loud and improved by Laszlo Biro in 1938. Slavoljub Eduard Penkala invented mechanical pencil in 1906 and the first solid-ink fountain pen in 1907. Felt-tipped pen, which was a predecess of markers and highlighters, was an invention of Yukio Horie from Japan. Roller ball pen, which uses water-based ink, appeared in 1963, also in Japan. Porous point pens that have points made from porous materials such as felt or ceramic appeared in 1990s. We today still use pens and pencils for writing and drawing as well as styluses (but those just on touch screens.

1.2 Development of writing instruments:

Table 1.1:

WRITING INSTRUMENTS	DEVELOPED YEAR
Metal Stylus	1300 BC
Reed pens	4th century
Quill Pens	700 AD
Wooden pencils	1795
Pens with metal nib	1800-1850
Fountain pens	1884
Ballpoint pens	1940
Felt-tipped pens	1960
Roller ball pens	1980-1990
Apple pencil	2017

1.3 Frequently used writing instruments:

1) Ballpoint pens:

It dispenses an oil-based ink by rolling a small hard sphere, usually 0.5-1.2mm and made of brass, steel or tungsten carbide. There are certain ballpoint pens combining multiple colours in a single based, the writer or artist may depress the tip with the desired colours.

Figure 1.1: Ballpoint pen

Characteristics of Ballpoint pen:

- Inkless starts.
- Gooping.
- Skipping.
- Burr strations.
- Uninked grooves alongside the main inked strokes.
- Trailing of ink alongside the main ink stroke.

2) Fountain Pens:

Fountain pens are old style of writing instruments. They have refillable or disposable ink cartridges. It is composed of a ink reservoir, from which ink flows through a small opening to the feed bar. Feed bar consists of an input capillary. The writing tip of the fountain pen consist of two points or nibs, which collectively result in one stroke of writing.

Figure 1.2: Fountain pen

Feature of Fountain pen:

- Nib marks (double tracks)- Presence of inkless furrow between two parallel inked tracks.
- Feathering of ink- A slow drying ink flowing from a slow moving pen on rough surface.
- Serated Margins- When the nibs of pen get rested due to action of ink.
- Pen scratches- Due to wear and tear of writing tip. Inadequate supply of ink to the writing tip.

3) Gel pens:

Commonly used water based gel ink that has a consistency between both ballpoint and roller pens. Ink is less likely to smudge. Compared to other inks, gel ink has higher viscosity, which supports a higher proportion of pigments in the medium. The pigments are opaque, and gel pens are available in several bright and pastel colours, as well as metallic and glittery colours which show up clearly on dark paper. Many of the gel inks are water resistant, and are not washed away by water once the ink has dried.

Figure 1.3: Gel pen

4) Graphite lead points:

Produce grey or black marks that are easily erased, but resistant to moisture, most chemicals, UV radiation and natural aging.

Principles of Graphite lead points:

Ratchet-based pencils have two or three small jaws inside a ring at the tip, which hold the lead. When though button on the end of the pencil is pressed, jaws move forward and open pushing the lead forward. Released button closes the jaws, but lead stays at the place because a small rubber device holds it.

Figure 1.4: Graphite lead point

5) Roller Ball pen:

It write with a thick vivid line. The line may smudge if you quickly run your hand over it.

Features of Roller Ball Pen:

- When used against a soft backing they leaves a pronounced central depression. Flow back seem to occur at the end of many strokes.
- The edges of the stroke are not sharply defined but are irregular and serrated.
- The pen is capable of producing changes in writing pressure more readily than porous tip pens. The typical action of fluid ink on the paper is present.

Figure 1.5: Roller ball pen

6) Marker Pens:

Marker pens come in four types of ink: pigment, water, oil and alcohol-based. Pigment and water-based inks are for traditional paper. On the other hand, oil and alcohol-based inks are for non-paper media (e.g. plastic, metal, or glass). These pens include permanent markers, non-permanent markers (e.g. dry erase markers), highlighters, and porous point (or felt tip) pens.

Figure 1.6: Marker pen

7) Stylus Pens:

Stylus pens are a two-in-one tool. One part is a traditional pen that writes on paper and the other part includes a stylus. A stylus has a round rubber tip that helps navigate touch screen devices. Some stylus pens come with a stylus at the top of the pen and others come with a stylus at the pen tip end. Scrolling, selecting, and highlighting are all made easier with stylus pens. Stylus pens also keep your screen free of fingerprints and scratches.

Figure 1.7: Stylus pen

8) Pencils:

It was first discovered in England in 1564. Pencil lead is made using graphite for blackness, china clay for hardness or polymer resins that give it strength and smoothness. The amount of clay, graphite and the period baking factors that determine the hardness of lead. It is much easier to produce a forgery with pencil than that with pen and ink, as pencil writings do not reveal the features such as pen lifts, pen position, retouching, pen stops.

Figure 1.8: Pencils

1.4 The writing instruments and their actions:

The pencil. (black pencils and/or colored pencils) possesses an unique non-flexible point, which was progressively worn out while depositing solid matter on the surface of the paper. When one writes with a very weak pressure on the pencil, the wear of the graphite point was slight, and the depositon on the surface of the paper is weak; the paper is not embossed, even if it lays on a soft support. Depending upon whether the point of the pencil is sharp or worn out, the light stroke will be more or less wide, but it will always be pale, the deposit of colored matter on the surface of the paper being very thin. When one writes with a very heavy pressure on the pencil, the wear of the graphite point will be significant, and the deposit on the paper surface will be greater, varying naturally with the hardness of the pencil. Whether the point of the pencil was sharp or worn out, hard or soft, the stroke will be more or less wide, but it will always be dark, the layer of colored matter on-the surface of the paper

being thick. Depending on the nature of the support of the sheet of paper, the paper will be more or less indented, showing relief on the back (embossing).

The kind of paper plays an important role in the formation of the different characteristics of the pencil strokes, because the type of the surface interferes with the formation of the layer of colored matter: a rough surface produces a greater wear on the pencil lead than a smooth one.

Pens exist today in different types and models. The old fashioned crow quill pen has disappeared, but there still exist ordinary steel pens which take up ink when they are dipped in an ink-pot; such dip pens exist in different models either with sharp or round points, or square points or lift up points. The most common pens to-day are the fountain pens, the nibs of which are more or less fine, but always rounded; such fountain pens contain their own ink reserve. The main and common characteristics of steel dip pens and fountain pens of that the two nibs are flexible and able to separate one from the other. The pens deposit a liquid ink which penetrates more or less into paper fibers and dries with air. When one writes with a very weak pressure on the pen, the nibs do not spread or spread very little, and the ink stroke is narrow; there is virtually no embossment on the back. When one writes with a heavy pressure on the pen, the nibs open proportionally with the pressure and their flexibility, so that one produces a wide stroke, and, depending on the nature of the support of the paper, it can create relief on the back.

The nature of the paper does not play an important role in the appearance of the ink strokes when the sizing of the paper is adapted for writing with ink.

Ball point pens have a hard, non flexible point; a small rotating ball which rolls the viscous ink on the surface of the paper. The viscosity of the ink varies from one manufacturer to another, and different ball diameters exist, When one writes with a very weak pressure on the ball point pen, only the top of the ball touches the paper and lays out a narrow stroke which is made up of a layer of coloured matter deposited on the ridges of the paper fibers. In such a case there is practically no relief on the back of the sheet, even if the paper lies on a soft support. When one writes with a strong pressure on the ball point pen, and if the support on which the paper lies is soft, the ball depresses the paper, producing a marked relief on the back. Under these conditions, the major portion of the ball touches the paper and lays out a wide stroke(the width of the stroke is naturally always less than the diameter of the ball itself) on the ridges of the paper fibers and, sometimes too, between the fibers in the furrows.

Fiber tip pens have a more or less sharp and flexible point which spreads out a liquid, quick- drying ink covering the paper fibers and flowing between the fibers. When one writes with a very weak pressure on the fiber tip pen, one produces a rather narrow stroke, depending on the sharpness of the point; there is, practically, no embossing. When one writes with a heavy pressure on the fiber tip pen, the result is quite the same; the stroke has the same width as the fiber point. There is also, practically, no embossing, even if the support is soft. It is important to notice that if the pressure on such an instrument is really very weak, one cannot detect any stroke at all, even if the point touches the paper.

1.5 Ink formulation:

Basic component of ink formulation are colorants, vehicle and additives.

1) Colorants:

It is a pigment or dye that gives desired colour to that ink. The light absorption and emission characteristics of the colorants play an important role in forensic analysis under analytical examination such as observation of ink under UV and infrared lights.

2) Vehicle:

It is also termed as carrier. Usually it is a solvent which allow colorants to flow on the surface.

3) Additives:

Additives have great forensic value because the compounds which are used as additive agents such as surface activator, fluorescence material, solubility enhancer, and corrosion controllers are specific for each manufacturer. The quality and quantity of additives used for ink manufacturing vary for one manufacturer to other.

1.6 Classification of inks:

On the basis of the nature of ink it falls into four categories

- Aqueous ink
- Liquid ink
- Paste ink
- Powder ink

1) Aqueous ink:

In this type of inks pigments or dyes are dissolved only in water in other words only water is used as a solvent in these types of inks .

2) Liquid ink:

In this type of inks organic solvent system such as propylene glycol, propyl alcohol, toluene, glycol ethers etc. Is used for dissolving pigments or dyes.

3) Paste inks:

In this type of ink solvents which used are hydrocarbons, alcohols, ketones and esters. Paste inks are viscous and tacky like adhesive.

4) Powder ink:

In this type of ink fine particles of pigments or dyes are in dry form. Solvent which are used in this inks are variety of organic substances like ethers, such as ethyl acetate, propyl acetate, butyl acetate and isobutyl acetate.

1.7 Nature:

The following type of inks are common:

- Indian ink:

It is a carbon suspension in water. The ink is made stable by the addition of glue. The colour is improved sometimes by the addition of Prussian blue. The ink was commonly used in Indian schools with Reed pens and by the petition writers in

writing important documents. The use of ink has decreased tremendously in the recent past.

- Iron tannate ink:

A mixture of tannic acid and gallic acid extracted from wood when mixed with ferrous salts, gives a colourless liquid when on drying and aging gives black colour. It is mixed with dyestuff to give proper shade. The common blue-black ink belongs to this class. It is a permanent ink.

- Dyestuff inks:

The most popular ink in these days are dyestuff inks manufactured from number of dyes, particularly from nigrosine dyes. They are available in all colour and shades. They are washable and are not permanent ink. They fade with time.

- Ball pen inks:

Ball pens have become very popular because of their convenience in use. Ball pen inks are dyestuff suspended in a suitable vehicle. Glycol are increasingly being used as vehicle in modern ball pen inks. All ball pen which uses ordinary pen ink has also been invented. It uses a sapphire tip contained in a platinum housing.

- Alkaline inks:

Alkaline inks are manufactured from dyestuffs and copper or vanadium complexes. They are quick drying and permanent inks.

- Special inks:

1. Printer's ink-It contains carbon, adhesive and drying oil.
2. Cancellation ink-It is used in post offices. It is similar to printer's ink.
3. Stamp-pad ink-It contains dyestuffs, glucose and glycerol or glycol.
4. Type writer's ink-It contains dyestuffs and oil (castor oil). It may contain carbon for permanency.

1.8 Forensic aspects of ink analysis:

Ink is used for writing, painting and drawing purposes. In many cases such as forgery, alteration etc. Investigating officers raised the questions about the origin and authenticity of ink.The most common task of forensic document examiner when such type of question is raised is to analyse the ink specimen by using scientific methods regarding findings . These scientific methods prove or disprove the authenticity of both disputed and standard inks.

CHAPTER-II

LITERATURE REVIEW

2.1 Ordway Hilton 1984.

This study focused on characteristics of erasable ballpoint pen. The ink of erasable pen differs significantly from that of the standard ball point pen, and for that matter from ink of all other modern day pens. In what way might this newer pen produce a written line different from other ball point pens? This is one question that the paper addresses with limited success. When erased, what techniques can be used to attempt to determine the text of the original writing? The writer considers all standard methods for deciphering erased writing and discusses modification by use of infrared film with oblique light photography — the method most successful in determining the original contents of the erasure.

2.2 James M.Egan, Kristin A.Hagan, Jason D.Brewer 2005.

Capillary electrophoresis with ultraviolet-visible photodiode array detection (190–600 nm) was studied as an alternative separation and identification tool for forensic ink examination. Two different buffer systems were designed to analyze dye compounds in various black ballpoint pen ink formulations. Results were compared to thin-layer chromatography experiments to evaluate the sensitivity and performance of capillary electrophesis. A database of ballpoint pen ink analyses and common-dye reference standards has been constructed for future forensic use. Capillary electrophoresis allows ease of sample preparation with the ability to separate and identify dye compounds based on a calculated electrophoretic mobility and a characteristic ultraviolet-visible spectrum. Protocols for capillary electrophoresis sample preparation were designed to closely mimic procedures already in place for common ink-evidence analysis. Because of the small volume necessary for analysis, the remaining solution could be further processed using current law enforcement procedures for confirmation.

2.3 BernhardSpengler, C Weyermann 2007.

The aim of this work was to study the drying process of ballpoint ink, characterised by the disappearance of volatile solvents from the ink entry. Phenoxyethanol is of particularly high interest as it is found in more than 80% of the blue ballpoint pens at different concentrations. Liquid extraction followed by splitless gas chromatography/mass spectrometry in the selected ion mode was used to measure the quantitative decrease of solvents from ink entries made with a blue parker ballpoint pen . In this paper we demonstrate that differentiation between fresh ink (<2 weeks) and older inks is possible under laboratory storage conditions.

2.4 Craig.D.Adam, Sarah.L.sherratt 2007.

This study focused on classification and individualisation of black ballpoint pen inks using principal component analysis of UV-visible absorption spectra. The technique of principal component analysis has been applied to the UV–visible spectra of inks obtained from a wide range of black ballpoint pens available in the UK market. Both the pen ink and material extracted from the ink line on paper have been examined. The complete set of 25 pens, interpretation of the loadings for the first few principal components showed that both the pen inks and the extracted ink lines may be classified in an objective manner and in agreement with the results of parallel thin layer chromatography studies. Within each class almost all inks could be individualised. Further work has shown that principal component analysis may be used to identify a particular ink from a database of reference UV–vis spectra and a strategy for developing this approach is suggested.

2.5 C.Wayyermann and R.Marquis 2008.

The study focus on differentiation of blue ballpoint pen by laser desorption ionisation mass spectrometry. Laser desorption ionization mass spectrometry (LDI-MS) may also be used for the analysis of dyes from ink. Ink entries on paper from 31 blue ballpoint pens have been analysed and their dye ink formulations compared. The pens were classified into 26 classes by LDI-MS. LDI-MS proved to be a more powerful method for differentiating ink formulations because it provides information about dye structures (molecular weights) and relative quantification of dye classes (peak areas).

2.6 H.Buchner, JH Bugler 2008.

The study based on age determination of ballpoint pen ink by thermal desorption and mass spectrometry . Two main approaches can be used for determining the age of an ink: indirect dating and direct dating. Indirect dating is based on the chemical analysis of an ink followed by comparison with known samples in a reference collection. This approach may allow for an anachronism to be detected. The second concept is based on measuring ink components that change with age. The analysis of solvents in ballpoint inks may be a useful parameter for determining the age of ink on paper. This age-dependent parameter was studied in 85 different inks ranging in age from 1 week to 1.5 years. It was found that some inks showed a significant decrease of this parameter up to an age of several months, and that the aging process can be monitored within this period.

2.7 Craig D.Adam 2008.

A novel approach to the non-destructive discrimination of black ball-point pen ink-lines on paper, has been developed which uses a standard luminescence spectrometer coupled with multivariate statistical analysis. The application of Principal Component Analysis (PCA) to these data-sets, followed by linear regression of the loadings, not only facilitates separation of the ink luminescence from that of the paper, but also allows a direct comparison between two ink lines on

documents. This data reduction means that such a comparison can be done on an effectively univariate basis whereby a straightforward statistical comparison is made between two numbers, each characteristic of an ink. Thus the question, in the forensic context, of whether two ink-lines are indistinguishable may be answered with a particular statistical confidence and the method shows significantly better discrimination, for the pens studied, than conventional forensic investigative techniques involving the luminescence imaging of writing using filtered light.

2.8 Magdalena Ezcurra, Juan M.G.Gongora,Rosa Alonso 2009.

This work reviews the different analytical methods that have been proposed in the field of forensic dating of inks from different modern writing instruments. The reported works have been classified according to the writing instrument studied and the ink component analyzed in relation to aging. The study, done chronologically, shows the advances experienced in the ink dating field in the last decades.

2.9 Francisco Alamilla, Carmen Garzia-Ruiz 2013.

The differentiation of blue ballpoint pen inks written on documents through an LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry and Multivariate Analysis) methodology is proposed. Small common office paper portions containing ink strokes from 21 blue pens of known origin were cut and measured without any sample preparation. In a first step, Mg, Ca and Sr were proposed as internal standards (ISs) and used in order to normalize elemental intensities and subtract background signals from the paper. Then, specific criteria were designed and employed to identify target elements which resulted independent of the IS chosen in a 98% of the cases and allowed a qualitative clustering of the samples. In a second step, an elemental-related ratio (ink ratio) based on the targets previously identified was used to obtain mass independent intensities and perform pairwise comparisons by means of multivariate statistical analyses. This treatment improved the discrimination power (DP) and provided objective results, achieving a complete differentiation among different brands and a partial differentiation within pen inks from the same brands.

2.10 Veronica.A.G, Isabella.C.F,Jorge.J 2014.

This study focused on Non-destructive identification of different types and brands of blue pen inks in cursive handwriting by visible spectroscopy and PLS-DA(Partial Least Squares Discriminant Analysis) for forensic analysis. Fast and non-destructive analysis of handwritten texts without any sample preparation. The method was developed based on twenty-five brands of inks from different blue pens. Standard samples were prepared to simulate the characteristics of the cursive handwriting. Reflectance spectra were recorded at different positions along a written line for each type and pen brand. The calibration set was optimized by the elimination of outliers and bias corrections. Two independent models were developed, the first one for identification of the pen type and the second one for brand identification. PLS-DA models presented mean prediction errors ranging from 0.03 to 0.11, which allowed the correct classification of all pen types and brands

studied. The method showed to be robust in relation to different paper types and batches of pens.

2.11 P Silva Ferreira, R Augusti 2014.

The study is based on forensic analysis of ball point pen using paper spray mass spectrometry. A novel analytical approach based on paper spray mass spectrometry (PS-MS) is developed for a fast and effective forensic analysis of inks in documents. Ink writings made in ordinary paper with blue ballpoint pens were directly analyzed under ambient conditions without any prior sample preparation. Firstly, the method was explored on a set of distinct pens and the results obtained in the positive ion mode, PS(+)-MS, demonstrated that pens from different brands provide typical profiles. Simple visual inspection of the PS(+)-MS led to the distinction of four different combinations of dyes and additives in the inks. Further discrimination was performed by using the concept of relative ion intensity (RII), owing to the large variability of dyes BV3 and BB26 regarding their demethylated homologues. Following screening and differentiation studies, the composition changes of ink entries subjected to light exposure were also monitored by PS-MS. The results of these tests revealed distinct degradation behaviors which were reflected on the typical chemical profiles of the studied inks, attesting that PS-MS may be also useful to verify the fading of dyes thus allowing the discrimination of entries on a document. As proof of concept experiments, PS-MS was successfully utilized for the analysis of archived documents and characterization of overlapped ink lines made on simulated forged documents.

2.12 Ricardo Saldanha Honorato, Anna De Juan 2015.

Fourteen commercial blue ballpoint pen inks from different brands and models were studied and Raman spectra were obtained on ink lines written on A4 sulfite paper. First, a study of the best Raman configurations, in terms of laser intensity used and acquisition mode, was carried out to ensure sufficient spectroscopic quality without damaging the sample. Chemometric methods were applied first to improve the definition of spectral bands and to suppress fluorescence contributions from the signal. Once the spectra were suitably preprocessed, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were applied to explore whether the different inks could be distinguished from their Raman spectra. The combination of Raman spectroscopy and chemometrics has been proven to be a promising fast non-destructive tool to differentiate among very similar.

2.13 Vishal Sharma, Raj Kumar 2017.

In the present work, fifty seven blue ballpoint pen ink samples were characterized by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy(ATR–FTIR) and discriminated on the basis of high performance thin layer chromatography (HPTLC) and ATR–FTIR spectroscopy coupled with multivariate analysis which otherwise seems to be alike and hence, undifferentiated. The approach of ATR–FTIR has proven out to be an effective tool for characterization of complex ink formulation and hence, ink's systematic discrimination with the help of multivariate analysis. The overall discrimination for

blue ballpoint pen ink with non–destructive analysis of ATR–FTIR come out to be 99.69%, which is highly significant in comparison to both visual inspection of the spectra (DP = 97.93%) and destructive HPTLC chromatography (DP = 93.80%). The similar methodology can be applied in the real case work of forensic laboratories to check whether two entries of ink on a sheet of questioned document have a common origin or not

2.14 Noppadon Nuntawong , Mati Horprathum, Viyapol Patthanasettakul 2018.

The study is based on improved discrimination of pen inks on documents by surface-enhanced Raman substrate fabricated by magnetron sputtering. The collected pen samples consisted of ninety-five blue and black ballpoint pens, of oil-, water-, and gel-based, indiscriminately acquired from local sources in Thailand. The Raman spectroscopic (RS) and SERS analyses were performed with the confocal Raman spectrometer at 785 nm excitation wavelength. The spectral data were directly collected from both the written pen inks and the traces of the inks with the SERS substrate. The results could categorized the pen ink samples into either the RS or SERS active/inactive results, and further calculated and analyzed as the discriminating powers (DP). The results indicated that the proposed SERS method was highly effective at distinguishing the ballpoint pens on the written documents with the obtained DP values at 0.79 and 0.92 for the blue and black pen samples, respectively.

2.15 Mason C Malloy, Milko Jaksic 2018.

The present study focused on determination of deposition order of blue ballpoint pen lines by MeV ion mass spectrometry.Secondary Ion Mass Spectrometry using MeV ion excitation was utilised for the analysis of optically indistinguishable intersecting ballpoint pen lines on paper. It was demonstrated that the technique was able to identify different colorants (dyes and synthetic organic pigments) with high efficiency and in a single measurement. The analysis of ink-ink intersections was performed using the Time-of-Flight mass spectrometer for MeV Secondary Ion Mass Spectrometry. This technique is attached to the heavy ion microprobe at the accelerator facility, and employs focused 8 MeV Si^{4+} ions for the surface analysis. Molecular imaging allowed for successful identification of sequence deposition order of otherwise optically indistinguishable intersecting lines.

CHAPTER-III

AIMS AND OBJECTIVES

AIM:

To characterise the different type of commonly used pen used in documents.

OBJECTIVES:

- To collect commonly used writing pens and extract the sample using Methanol.
- To identify the type of pen used in the documents by Thin Layer Chromatography(TLC).

CHAPTER-IV

MATERIALS AND METHODOLOGY

MATERIALS REQUIRED:

- Pre-coated silica gel G TLC plate, developing chamber, UV chamber, capillary tube, beaker.
- Chemicals
  - Methanol
  - Solvent system-Ethyl acetate : Ethanol : water (75:35:30)
- Specimen : Total number of samples used 10 blue and 10 black coloured commonly used writing pens.

Table.4.1: Commonly used writing pens, their colour and reference number.

MAKE	COLOUR	REFERENCE NUMBER
Cello Technotip	Blue	A1
Cello Technotip	Black	A2
Cello Pinpoint	Blue	B1
Cello Pinpoint	Black	B2
Montex Mega-top	Blue	C1
Montex Mega-top	Black	C2
Montex Smooth flow	Blue	D1
Montex Smooth flow	Black	D2
Linc Glycer	Blue	E1
Linc Glycer	Black	E2
Linc Pentonic	Blue	F1
Linc Pentonic	Black	F2
Rorito Fiberpoint	Blue	G1
Rorito Fiberpoint	Black	G2
Rorito Fastwrite	Blue	H1
Rorito Fastwrite	Black	H2
Doms Df ball pen	Blue	I1
Doms Df ball pen	Black	I2
Totem DL X	Blue	J1
Totem DL X	Black	J2

METHODOLOGY:

Ink analysis was done with thin layer chromatography and it can help to determine that whether there is any additions or alteration done to the contents of ink. Destructive techniques are useful for the determination of two inks on the same or different documents which are of the same formulation. Various methods such as thin layer chromatography, HPLC, GC etc can be used in ink analysis. In this project we used thin layer chromatography (TLC) for our analysis.

Thin layer chromatography:

- Sample preparation:

The paper containing ink sample was placed into a labelled test tube. Dissolved ink sample with 2 ml of methanol.

- Sample Application:

Handle the silica gel plate carefully. A line was drawn 2 cm from the bottom of the pre-coated TLC plate. Label on the plate with Reference number. Immerse the capillary tube into the sample. Make spottings on the TLC plate. Allow it to dry at room temperature

Development of the sample:

- Place the plate in the developing chamber. The solvent level must be below the spots. The solvent front moves slowly up the plate. Then the solvent front was 3/4 of the plate , remove the plate and mark the solvent front. Allow the plate to dry. Mark the visible spots by using a pencil. Calculate the R_f value. The sample was then identified with their respective R_f values.

RF value:

- When the solvent runs to a suitable height the plate was removed from the tank and allowed it to dry. R_f values are calculated by

R_f=distance travelled by the solute/distance travelled by the solvent.

Figure 4.1: Test tube with ink samples

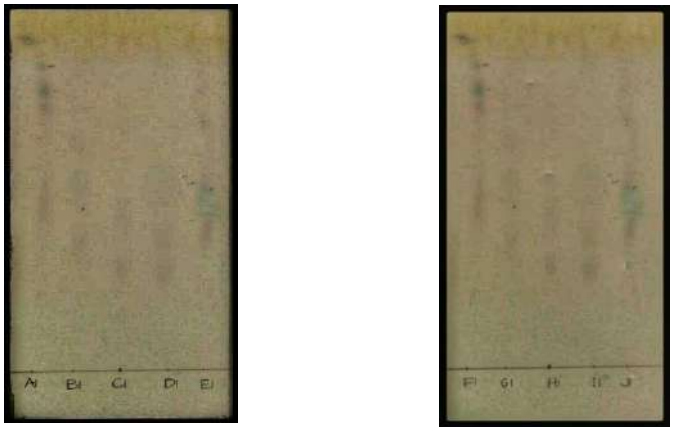

Figure 4.2: TLC of blue ink sample using solvent system Ethyl acetate: Ethanol: Water (75:35:30).

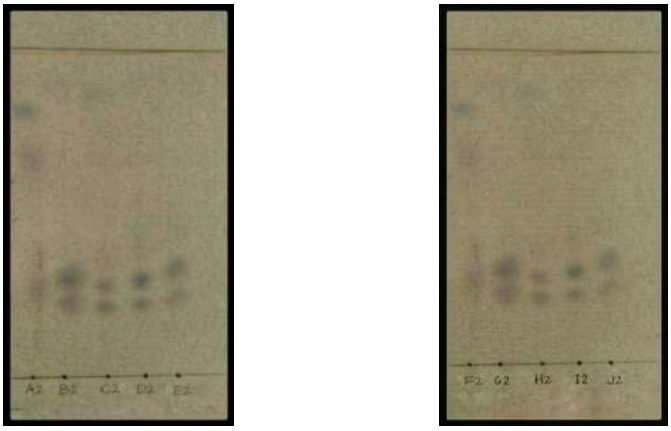

Figure 4.3: TLC of black ink sample using solvent system Ethyl acetate: Ethanol: Water (75:35:30).

CHAPTER-V

RESULTS AND DISCUSSION

Thin layer chromatography Examination:

Ink analysis is an important part of a document examination. It can be examined by different types of methods. In this study thin layer chromatography was done to study the type of commonly used writing pens to compare the ink of particular brand. 10 blue and 10 black commonly used pens such as Cello technotip, Cello pinpoint, Montex maga-top, Montex smoothflow, Linc glycer, Linc pentonic, Rorito fiberpoint, Rorito fastwrite, Doms DF ball pen, Totem DLX were selected. Extract the ink from the sample pen using methanol for the purpose of spotting on the TLC plate. The TLC was done by using the solvent system Ethyl acetate: Ethanol: Water (74: 35: 30). Place the TLC plate in the developing chamber. The solvent front slowly moves up the plate, then remove the plate and mark the solvent front and allow it to dry. The spots which is present on the plate is marked with a pencil. After the development of the plate each plate was individually visualized under UV chamber and R_f value were calculated by following formula:

R_f = distance travelled by the solute/distance travelled by the solvent.

Calculated R_f values of Blue and Black colour commonly used writing pens are represented below:

Table.5.2:-R_f value of commonly used pens

MAKE	COLOUR	REFERENCE NUMBER	R_f VALUE	AVERAGE
Cello Technotip	Blue	A1	0.53 0.51 0.53	0.53
Cello Technotip	Black	A2	0.42 0.40 0.40	0.40
Cello Pinpoint	Blue	B1	0.47 0.48 0.48	0.48
Cello Pinpoint	Black	B2	0.61 0.63 0.61	0.61
Montex Mega-top	Blue	C1	0.52 0.51 0.51	0.51
Montex Mega-top	Black	C2	0.73 0.75 0.74	0.72
Montex Smooth flow	Blue	D1	0.40 0.40 0.39	0.40
Montex Smooth flow	Black	D2	0.62 0.63 0.64	0.63

Linc Glycer	Blue	E1	0.26 0.24 0.24	0.24
Linc Glycer	Black	E2	0.36 038 0.37	0.37
Linc Pentonic	Blue	F1	0.30 0.31 0.31	0.31
Linc Pentonic	Black	F2	0.42 0.44 0.44	0.44
Rorito Fiberpoint	Blue	G1	0.52 0.53 0.52	0.52
Rorito Fiberpoint	Black	G2	0.58 0.58 0.57	0.58
Rorito Fastwrite	Blue	H1	0.43 0.43 0.41	0.43
Rorito Fastwrite	Black	H2	0.32 0.31 0.33	0.32
Doms Df Ball pen	Blue	I1	0.45 0.46 0.47	0.46

Doms Df Ball pen	Black	I2	0.31 0.30 0.31	0.31
Totem DLX	Blue	J1	0.48 0.49 0.49	0.49
Totem DLX	Black	J2	0.37 0.37 0.35	0.37

The above mentioned inks gave different chromatogram and R_f values of these inks were also different. By comparing the R_f values of the different brands of blue/black coloured pen itself gave different R_f values it may be possible to identify type of the pens used in questioned documents. Therefore, thin layer chromatography is one of the useful method to determine the writing instruments which is used in documents. It may be useful for the investigation of questioned documents, including forged checks, wills, or altered documents.

CHAPTER-VI

CONCLUSION

In India there are various kinds of writing instruments (pens) are available in the market. Identification and differentiation of type of source of inks used in these pens is key priority for the document examiners. Therefore, many documents are sent to the laboratory for ink analysis of the various type of ink present on the disputed documents.

In this study an attempt has been made to provide the R_f values of various brands of commonly used writing pens with two different colors. During this analysis we evaluated the R_f value of two different color of pens namely, blue and black commonly used pens. Using the destructive technique like TLC we developed different chromatograms and also studied their R_f value which can be used in future by the forensic document experts to compare the ink of particular brand .

Hence, it was concluded that with the help of this method we can prepare a set of standard data for different brands of commonly used writing pens. This could be helpful in future for the experts in establishing a relationship between two documents in case of forgery or ink analysis that includes a standard and a disputed document for its comparison. It may be also helpful in the analysis of different inks and their dye constituents.

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