

## Review: Techniques for the Characterization of Inks

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**Abstract:** Writing comprises writing tools to make documentation. With the advancement of technology, writing instruments have been developed in a phase wise manner and brought changes in ink chemistry. Recipes for formulation of inks have been modified over the years. Ink designed for use in different writing instruments or printing media have quite dissimilar components. There are occasions when documents used in criminal activities or in the course of civilization either alludes or created specifically for the purpose of deception. These kinds of many cases have been reported in the world of document examination. To solve this problem it is necessary to utilize some techniques chartering the document creation and history. The challenge faced by document examiners in such cases is to search for any clues that suggest that a particular ink entry was placed on the document some time other than indicated. Document examiners have invented methods for the scientific examination and identification of writing inks. Lawyers in the private sector and government agencies at all levels are using the examination of inks as a means of establishing the authenticity or fraudulent nature of questioned documents. The present review summarizes most of the available reports about the development of ink examination and identification techniques.

**Keywords:** TLC, UV, Vis, IR, NMR, SEM, GC/MS, SERRS

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### I. Introduction

The development for art of writing was growing stepwise with the reformation of civilization. It is a skill by which a person expresses his thoughts, ideas, feelings and emotions. Writing ability makes the human being a pioneer of the ecological system and sets him apart of this world among animal kingdom. This is the only talent that makes a person immortal by his valuable views which direct the society for its upliftment. Again, in advanced culture scripts, stamps, currencies, economic and legislation records, ledger and legendry etc. can only be possible by utilizing writing skills (1).

Writing comprises writing tools to make documentation using well distinguished language. Chemists, physicists, technologists provided writing tools like colorful inks, pens, brushes etc. to write on a substrate like paper, cloth, rock, wooden block, plastic or metal sheet etc. With the progress of technology, scientists invented superior tools in the modern society. Writing is an advanced mode to make the imagination to come true that one would arise preserved, secured and stable documentation. To achieve this target magnetic, electric, electronic inks are arising which will provide certainly a step towards conservative society.

The improvement of technology produced advanced writing instruments which have been grown in a progressive manner (2). The techniques modernized step by step through quill, fountain, ball, felt to gel pen and also in use as writing device nowadays. The successive variation of this technology pens also brought changes in ink composition and again to ink chemistry (3). Any liquid, semi liquid or solid material is named as "ink" that fulfill our purpose of writing, painting or drawing using writing instruments (3) on a substrate. A variety of ink recipes have been prepared using in writing tools invented in phase wise manner and after years and years they have been modified up to having quite different chemistry. Ink was used first by Chinese by mixing black pulverized stone powder in lake colors but the real ink was born in the third B.C. (4). Ink formulations in modern age contain many chemicals which are required to improve quality of ink. Modern inks are a complex mixture containing so many chemicals to impart some characteristic properties to it (5, 6). The colorants is to provide desired color to ink, is either dyes or pigments, a vehicle to dissolve colorant, may be either water or organic solvent and other ingredients like pH modifier to stabilized pH, humectants to hinder early drying, polymeric resin to bind ink to substrate and defoamer to adjust foaming capacity, wetting agents like surfactants to check film thickness formed by ink on surface and rheology, modifiers to command ink application, biocides and bacteriostatic to protect ink from bacteria and fungus which may produce fowl smelling (7,8).

On the basis of a colorant (dye or pigment) used, inks are classified as dye and pigmented inks (9). Similarly vehicle (water or solvent) used to manufacture inks also categorized the inks as aqua based and solvent based inks. Some additional chemical reagents used in pigmented inks which make sure strong adhesion of coarse molecules of pigment to the substrate and also then ensure prevent from being withdraw by mechanical abrasion. These components are typical resin in solvent based inks or binding agent in aqua based

inks. The usefulness of pigmented inks is that it will give highly intense colored marks on paper although using in less quantity. Addition of dyes can impart more strength than pigment in inks and able to produce varieties of colors and density per unit mass. Dye dissolved in solvent for preparing ink made it dry rapidly due to soaking tendency into paper. On the other hand dyes also made inks more sensitive to fade off on exposure to sunlight.

Although in modern age electronic communication, e-signatures, e-business, e-banking, e-money transactions etc. changes civilization and society, the paper documentation is also of great use and still a great problem in forensic sciences. These are occasionally generated to solve the purpose of deceptive incidents. Questioned documents can include diary entries, or whole diary, reconstructed files and false dated correspondence, prepared to show a particular sequence of events, occurred in the past or more simply a forged signature or an altered cheque. Subtle alteration to documents, such as papers involving medical malpractice, tax returns, will scripts and insurance claims, divorce judgments, copyright certificates, agreements related to labor management disputes, employee problem settlements and a variety of contracts etc. can have significance financial implications. These kinds of many cases have been submitted by a number of crime reporters or document investigators. Principally the determination of entries on a document are whether similar or not, will be of greatest interest (10). This allows the determination of whether entries have been added or altered. Different types of ink have slightly different chemical composition so can be readily distinguished by comparative microscopy or chromatographic methods. The dating of documents and writing is another issue in the evaluation of authenticity. To solve this problem it is necessary to utilize some techniques chartering the document creation and history. The job of document examiners is very challenging to catch defaulters by searching clues that suggest that a particular ink entry was placed on the document some time other than indicated will provide a ground to prove any ink entry on the document as false or introduced to deceive.

Physical or chemical are the two approaches for determining the age of inks or date of script creation (11). By one the measurement and comparison of ink compositional characteristics (static determination) of suspected script inks with the collected samples of inks existed when the script written, is processed. While in other estimation of aging (dynamic determination) properties of ink is carried out. In the static approach the examination of such characteristics of ink is taken in to consideration which do not changes with time or age. This can be done by matching tagged properties by manufacturer or consulting files of ink manufacturers that if the ink was produced at the time when the script was written. If script ink was assigned to be not available when it was created, the document was declared as illegal or false. But there is limitation with adopting this approach that many of the ink formulations do not have any tag and also records are not maintained by the manufacturer (9).

The methods which determine the change in various properties of ink with time period (12) is a dynamic approach and termed as "ink dating" (13-15) and are also sometimes applicable to so many cases. The dynamic approach measurements may be non destructive or destructive (16). Ideally non destructive, comparative techniques are used to distinguish between different inks in documentations. Although inks may be very similar to human vision, they can be very different if examined in the infra red region radiations or when illuminated by high energy light at specific wavelength which excites fluorescence, the degree of variation relates to the chemical composition of the ink. The processes in which documents remain preserved and undestroyed are called as non destructive technology such as ultra violet, visible and infrared spectroscopy and luminescence, photography and photometry etc. However, these techniques are limited and suffer from insufficient discriminating power to allow the differentiation between similar inks from the same manufacturer. This problem is becoming more challenging as sophisticated writing and printing technologies are evolving. Hence, further destructive techniques are now frequently necessary to provide a more rigorous comparison. These techniques can be carried out on a relative thing like amounts of ink, taken to grow the pen line of a single character; therefore, extraction methods are used for identification of inks. The methods applied effectively to this type of analysis have included chromatography and electrophoresis. These are exclusively used for the separation and comparison of different constituents in inks.

Document examiners have invented methods for examining and identifying writing inks scientifically. Lawyers in the private sector and government agencies at all levels are using these methods of ink examination to decide the true or false nature of questioned documents. This present review describes the analytical techniques for ink examination and identification reported in literature surveyed by us.

### **Analysis of inks**

The complex nature of ink formulations used for writing and printing was developed phase wise as new inventions of writing and printing tools grew. Scientists made efforts to identify these upcoming inks with accuracy on the basis of their physical and chemical characteristics.

### **Writing inks**

The forensic analysts utilizing a number of techniques to analyze writing inks comprise studies in which the ink of suspected documents has been compared with inks analyzed previously by investigators. Ancient methods for ink characterization were developed earlier for iron gallotannate inks utilized to write documents primarily (17-19). "Iron galls" the name given to these primitive inks which were used with quills to fountain pen upto the early 20<sup>th</sup> century, when formulations for fountain pens like blue-black and modern washable inks were originated (20). Afterward the blue black and washable ink recipe were employed with in the fountain pens. The dating of the ancient manuscripts written with iron gallotannate inks were carried out by Auger microscopy in which iron atom migration towards the outside from ink boundaries was estimated. As the age of ink increases, migration of iron atoms also increases exponentially (21).

Ballpoint pens were first introduced in 1939 abroad and in 1945 in the USA and ballpoint pen inks changed on many times to obtain existing one. To reduce smudging in 1950, ballpoint inks changed to a glycol from oil base. Metal chelate dyes like blue green copper phthalocyanine, the most frequently used due to its solubility. Nowadays copper phthalocyanine is preferred to use as a cyan colorant behave as a soluble dye or an inorganic pigment in all over the world. It contains heavy metal copper easily to detect in ink samples.

Gel pen inks were come in light in the end of 1980. They were different from ballpoint inks in aspects they are composed of colored pigments containing carbon black in place of organic soluble dyes. The pigments from gels or aqueous suspensions being insoluble hence inks are now defined as gel or aqua suspension but not as liquid. The forensic experts has applied techniques like filtered light examination (22), thin layer chromatography (23), Scanning electron microscopy (24) and Raman spectroscopy (25,26) to identify these with moderate success. Later Scanning electron microscopy (SEM) has also appeared to be a strong recent characterizing method for gel pen inks (24). It establishes complex morphological structural changes of numerous gel pen inks which is quite different from so many other writing inks.

### **Printing inks**

The classification of inks from printing media are made as-

- (a) Traditional and contact inks (impact media): It comprises typographic, offset lithography, gravure, intaglio, flexographic and screen, and
- (b) Digital and noncontact inks (non-impact media): It includes inkjet inks, electrographic toners and thermal inks.

### **Traditional printing inks**

The inks used in traditional printing or in impact media have very much difference with the inks that used either in pens or in non-impact printing media, in sense that because they are generally oil-based and used high pigment content, inorganic in nature. Suspected documents produced using either offset inks by intaglio, lithography or typographic printing machines processes are diagnosed easily by forensic experts. The organic constituents of such inks are resins, solvents, binding agents, oils, etc., whose identification can be carried out by techniques like infrared spectroscopy and pyrolysis gas chromatography-mass spectrometry. In the same way the inorganic portions such as pigments, carbon black, metal containing additives were also identified by other processes like atomic absorption, inductively coupled plasma-mass spectrometry, electron beam-x-ray generating techniques such as scanning electron diffraction spectrometry, x-ray photoelectron spectroscopy, Auger electron spectroscopy and x-ray fluorescence (27).

### **Digital printing inks**

The digital printers and photocopier machines are utilized in official or personal purpose. These are mostly involved in criminal and illegal activities and became a challenge for forensic experts for a long period. Some quality techniques were widely emerged by scientists to identify and characterize them are investigating inkjet inks and electrophotographic toners used in printers while printing as under-

### **Inkjet inks**

The inkjet ink formulations are manufactured keeping in mind the needs of the printing methods like secretion in bulk, storage in printer head, droplet creation and outcome delivery, soaking by the paper fiber, fixation and drying. Inks are manufactured obtained necessarily from 2 to 10 cP. Inkjet technology generated prints if inks are well soaked by the fibers of substrate paper (28).

The most common practical process to identify inkjet inks chemically is thin layer chromatography (29) which is the most important for color printing inkjet inks. These contain dissolved dyes as colorant (30). Many reports are available in literature in which mass spectroscopy was used in coordination with pyrolysis gas chromatography (31), desorption ionization (32) and laser ablation inductively coupled plasma method (33) to discriminate inkjet inks. The most recent technique to ascertain the molecular structures and configuration

complicated dyes constituent of ink was found Raman spectroscopy (34). This has been provided a powerful method to characterize inorganic metallic pigments in inkjet ink as colorant by examining pigment particle shape, size, morphological features and chemical composition. Raman spectroscopy has been proved to be a valuable analytical tool for characterization of inkjet ink formulation (35).

### **Solid inks**

Electro photo graphic toners are solid dry powder, applicable for desktop printing by xerox and fax machines. Nowadays, these are formulated by the combination of pigment, dye and resins in solid form having 3-20  $\mu$  sized particles but these are also obtained using chemical methods and named as chemically prepared toners (CPTs) which exhibit nano sized particles. To prepare toner, limited sized solid colorant mostly dyes and sometimes colored pigment is mixed with wax and polymeric resin as dry solids. There is also a need to mix some additives in minute quantities to assure best performance which are flow promoters, agents for charge coupling and cleansing agents for printer drum.

The ultimate shape of toner particles are determined by large organic polymer component, especially in the CPTs. Grinding-milling process is carried out to manufacture toners containing fine particles whose average size is less than 10  $\mu$ , exhibit random sized distribution particles, with high concentrations of above and lower concentrations of below average sized particles. The CPTs with nano sized particles are obtained from chemical polymerization and solvent exchange methods, yielding more homogeneous fine particles of uniform size and shapes which perform quality printing (36). The manufacturers also provides tagged data pack describing morphological parameters and toner particle size so that user can monitoring of quality of their hard copies (36).

### **Techniques characterizing inks**

A number of techniques described by researchers and technologists are summarized as under-

#### **Chromatography**

The comparison of writing inks has been made possible by the introduction of chromatographic methods which impact on the detection of fraudulent documents. Some of chromatographic techniques reported in literature used for analyzing inks are as follows-

#### **Paper chromatography and paper electrophoresis**

These were classified as oldest and primitive methods, used for analyzing inks. It is a destructive process performed to analyze inks and used particularly for inks containing organic dye as colorant (37). Characteristics of inks have been identified by traditional electrophoretic methods (38, 39). Chromatography works on principle of less or more differences in solubility and distribution coefficient of dye between different solvents. Similarly inks has also been characterized by electrophoresis (37), in which charged chemicals are forcefully made to be mobile with an average speeds towards the opposite signed electrode by applying electric fields on their path so that ionic substances will be able to move to the electrode of opposite sign by adjusting their environment.

In paper chromatography (35) technologists used either single solvent or solvent mixture such as ethyl acetate, lacquer thinner and ethyl alcohol (10:1 v/v), nitroethane and nitroethane with ethyl alcohol and lacquer thinner. No single solvent or combination of solvent is found to separate all dyestuffs in the inks. Scientists classified ink dyestuffs into types, varieties, or groups according to their dyeing and chemical properties on the basis of results obtained by performing some preliminary tests in which their reaction were carried out with certain chemicals. For example, phthalocyanines produced a bright green color with hydrochloric acid and sulfuric acids, while ignition of the copper containing dyestuff gives a green flame due to copper. Victoria blue develops a brown coloration with both acids and bases. Rhodamine B was not affected by base while faded to yellow orange with acid. This dye fluoresces to bright pink under the influence of ultraviolet radiations. Eosins with sodium hydroxide changes to orange color and faded to yellow with hydrochloric acid. All the results obtained from above experiments will provide scientists an idea to develop a plan identifying and characterizing ballpoint inks.

#### **Thin-layer chromatography (TLC)**

The technique of chromatography which is found to perform the easiest, simplest resolution and also widely used, called as thin-layer chromatography (TLC) in which there are two phases. One is the stationary phase, a layer of powdered solid materials sticking to a plane surface of a plastic, aluminum or glass plate. The samples are placed as spots on a line drawn 1 cm above the bottom of the plate and placed in a chamber vertically containing either a pure solvent or a mixture of solvents named as the mobile phase that run upward over the stationary phase on plate to a remarkable height. As mobile phase moves up, it also allows migration of the samples placed at original line. After a certain period the plate is then removed out from chamber, dried, and

observed either under visible light or by exposing to a ultraviolet (UV) light. One or more spots of characteristic colors may be seen or sometimes spots are developed to visualize by spraying a chromatogenic reagent compounds of sample due to chemical changes having different retardation factor ( $R_f$ ) values which is defined as the ratio of distance traveled by the separated compound to the total distance traveled by the solvent front from the original drawn line bearing sample spot. The factors affecting  $R_f$  values of a compound are the material used as the stationary phase and solvents used as developing liquid. The  $R_f$  values can provide qualitative estimation of a compound and quantitative estimation can also be carried out by measuring density of the separated spot of that compound (40-42).

A renewed technique was developed by Kurnaz (43) allowed better separations with dyestuffs having same  $R_f$  values which were previously not completely separated. To solve such problem, he removed the silica gel or cellulose layers carefully from the underlying plate and produced a different result than the previous one as whole of the eluent travels through the sample spot and it will give a series of discrete bands in place of overlapped bands. This technique was successfully used to separate dyestuffs of inks which were having difficulty in separating with the standard method (44). After that novel TLC method for analyzing ink dyestuffs in which the samples of inks were separated primarily by one reagent grade solvent like n-butanol, ethanol, ethyl acetate and then with pyridine. The silica gel coated plate in absence of fluorescent indicator was used. Two solvent systems either ethyl acetate: absolute ethanol: distilled water (75:35:30 v/v), or n-butanol: ethanol: distilled water (50:10:15 v/v) were used. The results indicated that the used two solvent systems were quite efficient for separating the dye constituents of most of the ink samples studied.

Crown et al. (45) identified most of the inks using TLC technique. They dissolved ink sample in pyridine and placed on silica gel plate and then allowed to run in solvent system of ethyl acetate: ethanol: distilled water (70:35:30 v/v) to resolve dyes from most of the inks but for some of the samples they used Merck silica gel plates running with a solvent system containing n-butanol: ethanol: distilled water (50:10:50 v/v). 720 inks of different brands were examined using these two TLC system separations effectively and successfully.

Brunelle et al. (46) made comparison over 150 typewriter ribbon inks of seven different brands by thin-layer chromatography. The ribbons after cutting into small pieces were extracted with pyridine for thirty minutes. The development of TLC chromatogram was carried out in two steps process. In first step solvent mixture of ethyl acetate: ethanol: water (75:35:30 v/v) was used, and the second step was taken with n-butanol: ethanol: water (50:10:15 v/v). The development of chromatographic plates was employed for thirty minutes in first step and for sixty minutes step and after these two steps plates were dried. All of the samples have been easily differentiated by the application of either only one or both of the steps.

TLC analysis was further adopted by Verma et al. (47) for analyzing fibre tip pen inks. Twelve sign pen inks from three brands have been procured from the market and were identified using silica gel plate on which the ink samples were spotted on after dissolving in ethanol. Two solvent systems were used, first, a mixture of butan-1-ol: acetic acid: water (6:1:2 v/v), and other butan-1-ol: acetic acid: water: 1,4-dioxane (6:2:2:1 v/v) and using above two solvent systems they were able to characterize all inks by calculating their  $R_f$  values for the resolved components on the TLC plates by which ink samples were successfully compared and discriminated. Under ultraviolet radiation the inks of orange, pink, red and crimson colors fluoresced provided more valuable information to identify these inks after separating their constituents by TLC.

Infrared luminescence photography of TLC chromatogram for inks of the same brand was obtained by Blackledge et al. (48) to differentiate them. They used three types of commercially available TLC plates that were Merck, Type 5719 glass backed TLC plates, silica gel 60 F 254 precoated, 5 cm × 10cm, 0.25 mm layer thickness; Merck, Type 5549 TLC aluminium sheets, silica gel 60 F 254 precoated, 5 cm × 7.5 cm, 0.2 mm layer thickness and Merck, Type 5556, HPTLC aluminium sheets, silica gel F 254 precoated for nano-TLC, 5 cm × 7.5 cm, 0.2 mm layer thickness. All of these were used without any pre treatment. Four solvent systems were used differently which were ethyl acetate: ethanol: water (70:35:30 v/v), Butan-1-ol: ethanol: water (50:10:15 v/v), Acetone: water (2:1 v/v) and Butan-1-ol: ethanol: water: acetic acid (18:2:2:1 v/v). A well distinguished separated component was seen after running spotted plates by the all four solvent systems, but no differentiation between the inks could be made. One or more extra luminescent compact bands were produced on foil backed plates by using infrared luminescence photography and able to point out differences among pen inks. They made conclusion that thin-layer chromatography followed by infrared luminescence photography is an important technique to differentiate between two inks in cases where no other method was able to provide evidence.

Olsen and Hopson (49) performed studies for identification of writing inks using TLC as a validated technique to separate constituent dyestuffs and evaluated  $R_f$  values for proper comparison.

Ordidge et al. (50) analyzed stamp inks using TLC on passports black and white photographs (Kodak Bromide), developed (Kodak D-163) and washed by the standard procedure. They were then clipped on white card and using fluid with fibre tipped inks, lines were drawn across the card and photograph. Using ballpoint pens, the formation of marks on photographic emulsions is a quite difficult task. These photographs were kept as such for one year in the dark partly exposed to light. Afterward microscopic examination was carried out to

assess color. Infrared luminescence and reflectance were recorded photographically. The extraction of stamp ink from the passport was done by a solvent mixture of pyridine and water (1:1 v/v). High performance thin layer chromatographic plates obtained from Merck were used and the solvent mixture of butan-1-ol, ethanol and water (4:1:1 v/v) was utilized. The results were observed with closed circuit television systems. They obtained successful separation of dyes from five black fibre-tipped pen inks, five blue-tipped pen inks, five fluid pen inks and two black fluid pen inks by this TLC system. They come to the conclusion that extra care must be needed to obtain precise results from thin-layer chromatography from photographic paper, and samples might only be possible to differentiate if there were gross differences in the number, color and Rf values of the dye constituents.

Lyter et al. (51) has performed work on his own idea that identification of inks might be assessed with required instrumentation as adjuncts to TLC including video scanners, charged coupled detector (CCD), and also reflectance spectrophotometer. Inks were dissolved in methanol and chromatograms were developed using a solvent mixture of ethyl acetate:ethanol:water (14:7:6 v/v) as in usual TLC. Then adjunct instrument was used to discriminate resolved spots on TLC plates. The color specificity and resolution were two factors, evaluated by them. They noticed that scanners were not able to resolve constituents sufficiently if the scan time is small, but may be improved on increasing scan time while densitometry was proved as an accepted technique in analyzing different colored constituents.

Some pigments poses very low solubility in some solvents. Such pigments were also studied using TLC by Aginsky (52). In his research he incorporated samples of hundred and twenty synthetic pigments and dyes, writing and printing inks and toners for copying machines. The inks from scripts were removed by scratching or cutting with help of a safety razor and then extracted which were then dissolved in the strong polar solvent such as dimethyl formamide, but pigments were found to be insoluble in it hence they were solubilized in concentrated sulfuric acid. TLC separation was conducted first with eluent chloroform which produced chromatographs of aqueous dyes but not of oil soluble and ethanol soluble dyes. TLC chromatograms of basic, acidic, oil soluble, ethanol soluble and water soluble dyes were developed with the solvent mixture ethyl acetate:isopropanol:water:acetic acid (20:15:10:1 v/v). Concentrated sulfuric acid as an eluent was utilized for TLC separation of inks constituting phthalocyanine and other slightly soluble organic pigments which was proved very successful for separating dye constituents of writing inks.

A fast and new approach was originated by Djozan et al. (53) in which inks from questioned documents were differentiated by developing TLC chromatograms using silica gel 60 coated plastic sheet as stationary phase without fluorescent indicator and a mixture of ethyl acetate:ethanol:water (70:35:30 v/v/v) as mobile phase and then designed specific image analysis to software by making data acquisition for evaluating TLC plate development. To differentiate among different pen inks they designed new software on the basis of intensity profile of red, green and blue (RGB) characteristic. The ordinary office scanner was used to scan the developed chromatograms to discriminate among different pen inks. Intensity profile of RGB characteristics for each sample were produced and compared with this newly developed software. RGB profiles of different inks indicated that the patterns in most cases were distinctly different from each other. This method allowed discrimination among different pen inks with a high reliability and its discriminating power is found as 92.8%.

Houlgrave (54) carried out experiments for resolving writing ink samples from ballpoint pens using TLC to compare and characterize them. Chromatographic profiles developed on a TLC plate and evaluated with surrounding light, by which different or the similar ink formulations appeared indistinguishable on observation using filtered light. It can give very effective various illuminations of ink characteristics that are not readily appeared with ambient light. There may be a chance that some of the components among a mixture in writing inks respond to characteristic wavelengths of radiation which are not visible to the naked eye. Further evaluation using an alternate light source coupled with the appropriate filter proved to be an effective means for definitive discrimination.

#### High-performance liquid chromatography (HPLC)

The mobile phase is either a liquid or a mixture of liquids in high-performance liquid chromatography (HPLC) (55-57) which is forced to travel through a column under pressure, exerted using a pump. The Stationary phase, packed in stainless steel tube or a glass column uniformly with spherical or irregular shaped porous silica particles whose size was in  $\mu\text{m}$  range. The eluent was allowed to pass through column and lastly through a detector which separated components and passed to monitor them. The strength of bonding of different chemical groups to the surface of the silica particles estimates the mechanisms for separation in liquid chromatography. The stationary phase is relatively more polar and the mobile phase is relatively non-polar in normal liquid chromatography but a non-polar bonded stationary phase and a polar mobile phase is used in reversed phase liquid chromatography. The differences in the partition coefficients of components between the stationary and mobile phases result the separation of constituents. The polarity of liquids used for mobile phase must be largely different from the liquid used for the stationary phase. It makes the two liquids immiscible. An

isocratic elution is called if a separation employs a single solvent system. Separation efficiency can be highly increased by gradient elution containing two or more solvent mixture differing especially in their polarity. The ratio of the two solvents is varied in a preplanned manner after beginning of elution, sometimes it is needed continuously and sometimes in steps serially. The stationary phase is an ion exchange resin in ion exchange chromatography and separation is dependent of the strength of the attractive forces impart between solute ions and the ionic exchanger free valences on the resin. The stationary phase is a wide pore gel in size exclusion chromatography which can separate molecules according to their shape and sizes, the smallest molecules travelling most slowly through them. Scientists reported (58-61) that UV, infrared absorbance, fluorescence and mass spectrometric detectors are used in HPLC analysis.

A novel method was reported by Liu et al. (57) to ponder false entries on document written with the black gel pen were illustrated for classification and dating. The technique was based on ion pairing HPLC. They divided ninety three black gel pens into two classes- dye based and pigment based on the basis of results obtained by preliminary solubility test. An ion pairing reagent tetra butyl ammonium bromide (40 m mol/L) was used to separate dye constituents. Dye components were classified on the basis of their number and chromatographic retention times of the main dye constituent. The changes in chemical composition of the dye components constituting the black gel pen ink entries on substrate were studied in light and natural aging circumstances and noticed that dye constituents decomposed and their extent of decomposition related to the aging was measured.

For characterizing writing inks the application of high performance thin layer chromatography (HPTLC) was invented by Tappolet et al. (62). The Merck silica gel plates were dried at 60°C for one hour and diluted fountain pen inks to 1:5 (v/v) before application to the TLC plates. For ink samples they attempted experiments to decide the best solvent mixture resulting a quality separation of the dyes with reproducible chromatograms and concluded that the solvent mixture of iso-butanol:ethanol:99% acetic acid:distilled water (20:5:5:10 v/v) was proved the best for black and blue black fountain pen inks, ethyl acetate:ethanol:distilled water (70:35:30 v/v) for blue and red ballpoint pen inks and they also estimated the relative values for TLC and HPTLC. They found that HPTLC had some benefits over the TLC which arise rapid development of chromatograms, increased sensitivity with small quantity of sample and better resolution of components with greater reproducibility.

Colwell et al. (63) was successfully discriminated ballpoint pen inks using HPLC technique. The sample is extracted from the paper with written line by 10 microplugs punching with the help of a syringe needle. All constituents were separated on a 25 cm long and 10  $\mu$ m in diameter, column of silica gel and using a mobile phase of 2% formamide in methanol. Ballpoint pen inks were easily differentiated on the basis of presence of the different dyes or sometimes on the relative dye amounts. Scientists specially mentioned the ability of this method based on the types of vehicles present on recording the ratio of vehicle (resins, viscosity adjusters etc.) to the dye. The direct analysis of vehicle components was also performed using a mixture of 2% isopropanol in heptane as a solvent system and the detector monitored constituents at wavelength of 254 nm. Researchers invented the effect of various kinds of papers on which inks deposition could occur to note that it make any interference in detection using visible or UV monitoring. None of the interference was noticed on the chromatograms for any variety of the papers used for experimentation in either the visible or UV range. Also, no interferences in the chromatograms were observed even using the weaker condition of solvent extraction. The different samples were produced chromatograms with reproducible retention times and relative peak heights of all of the dye peaks. However, it was found more difficult to differentiate two inks which had the same dyes but different in their relative amounts than for others which contained different dyes. The characterization of the various inks was positively made on the basis of relative peak heights of the bands. Some work also conducted in which the solvent conditions used for ballpoint pen inks were too strong and not allowed separation in felt tip pen inks and a weaker solvent system i.e. dichloromethane, ethanol and formamide (89:10:1 v/v) was found more suitable for inks used in felt-tip pens.

HPLC was attempted for examining ten different ballpoint pen inks (64) that were not possible to differentiate by TLC. Three samples of ten plugs each using a hypodermic needle was removed from written documents and extraction was carried out with 20  $\mu$ l pyridine. Finally a 10  $\mu$ l aliquot of the extracted sample was introduced into the HPLC system. The used mobile phase was a mixture of acetonitrile, 0.005 M Pic B-7 water solutions (80:20 v/v) at a flow rate of 2 ml per min. The  $\mu$  Bondapak C-18, 30 cm\*3.9 mm i.d. was used as column. Detection was carried out by a dual wavelength ultra violet or visible detector monitoring at 254 and 546 nm. Due to the complexity of chromatograms at 254 nm a wavelength of choice to compare was taken as 546 nm. The success of the work was that the system used for HPLC was found capable of quantitative and qualitative differentiation of all ink samples which were not able to differentiate by previously existed methods including TLC. With the help of rationing of peaks, different peaks were compared with the largest peak given a value of 100%. The quantitative differences were evaluated a maximum deviation from the mean of 2.0% was found between three of the injected samples. Researchers also commented that paper type also showed an effect

on the extraction of a given ink formulation. The heights of peaks were enhanced on increasing the size of sample from 5 to 10 microplugs and enhancement in peak heights was exponentially increased with increase of sample size from five to ten microplugs, produced peak greater in heights and the increase in peak height was equivalent to the increase in sample size. Investigation of the analysis was also performed four different batch samples of a single ink which resulted that corresponding peaks were qualitatively similar but quantitatively different. The quantitative differences could be observed associated with the reproducibility variation and different types of paper used.

Keto (65) performed studies for characterizing alkaline blue pigment in counterfeit currency using HPLC. The identity of alkali blue pigment is Pigment Blue 19, having color index no. 42750:1, is an organic synthetic one which was mainly incorporated with black letter press and offset inks to decrease the brown undertone of the primary pigment i.e. carbon black. The single batch of pigments from different brands were divided into ten samples and all dissolved in methanol and finally separated through a column i.e. micro Bondapak C-18 reverse phase 30 cm\*4 mm i.d. with eluent contained methanol/ water (1:2 v/v) (I) and 100% methanol (II). A linear gradient elution program of 10% (II), 90% (I) to 100% (II) in 15 minutes was utilized. Statistical F and T tests were used for the data evaluation. From the F test results, the researcher concluded that different brands showed greater variability within samples than between the same brand. A T test was applicable to the retention times for each and every peak obtained on the chromatogram. Two-sided retention time tolerance, at 95% confidence level intervals contain the given chromatographic constituents in 95 out of 100 resolved samples of alkali blue. The obtained tolerance intervals can be reflected as a measure of the chromatographic separation, included preparation of solvent, gradient formation and column degeneration. All retention times on the chromatograms for eluted peaks were found to exist within the tolerance intervals of retention times.

A process for the separation of basic dyes using a novel HPLC system monitoring by a photodiode array detector was attempted by Griffin et al. (66). The Standard dyes were procured from Ciba Geigy Company and the packed column with Phase Sep Spherisorb silica (5 µm) was used. The eluent was prepared by mixing an aliquot of 94 ml concentrated ammonia, 21.6 ml of concentrated acetic acid in 884 ml of distilled water and then adjusting its pH to 9.76 using either concentrated acetic acid or concentrated ammonia. To separate twenty one commercial basic dyes a buffered (pH 9.7) and silica column with an eluent of water-methanol was used. Better results were obtained using a gradient elution program which varied the buffer concentration and identification of the different components either resolved or not resolved during HPLC separation, has been successfully carried out using the photodiode array detector coupled with a NEC-APC III computer.

An optimal HPLC system differentiating and identifying acidic dyes with multi-wavelength detection and absorbance ratio characterization has been developed by White et al. (67). They used for HPLC 5 µm polystyrene-divinyl benzene (PSDVB) as column packing material and a solvent system of acetonitrile:water (50:50 v/v) containing 0.7 g/L of citric acid and 3.396 g/L (0.01 M) tetra butyl ammonium hydrogen sulphate (TBAH) were used. The pH 9.0 of solution was fixed by the addition of concentrated ammonia solution drop by drop. He adopted traditional method with single wavelength HPLC determination and concluded that the determination of retention time for a component was basis of its qualitative analysis. However, with inks constituting a large group of complex constituents, the differentiation was very poor yet it was possible to execute a sample differentiation to higher degree, by correlative retention times and absorbance rationing procedures. The requirement of absorbance rationing process is that several wavelengths must be settled to monitor by setting a multi-wavelength detector. The pilot wavelength is chosen as color of the dye solution appeared e.g. yellow or green, 400 nm; if the color is orange, pink or red, 500 nm; and for purple color, 590 nm selected as the reference wavelength in order to get absorbance ratio data. Finally the ratios of other absorbance wavelengths to the reference were evaluated. Through the experiments researchers got results for fifty two dyes and all were successfully differentiated except from different salts of the similar dyes and using the absorbance ratio data, even if the samples showed similar retention times and colors were also discriminated.

Tebbett et al. (68) differentiated non-ballpoint pen inks after performing a series of experiments by using HPLC with multi-wavelength detection and estimated that like ballpoint pen inks, non-ballpoint pen inks also composed of two major fractions i.e. colored and uncolored. The colored fraction contained different types of acidic and basic dyes which used in textile industries. Tebbett concluded that two major problems were here for analyzing inks that were the lack of sensitivity, originate requirement to use approximate 1 cm of an ink line, and it have to monitor single wavelength it must be needed to repeat analyses at various wavelengths in order to detect sufficiently the different dye components. According to them, multi wavelength detection must be necessary for ink analysis. Using HPLC, as a selection of solvent systems were evaluated for their ability to differentiate the seventeen non-ballpoint pen inks. Researchers have been analyzed hundred and thirteen various non ball point pen inks and they classified them into seventeen sub groups on the basis of TLC analysis. Tebett et al. extracted ink dyes from paper using HPLC mobile phase solvent system and they separated them using Spherisorb 5 µm C-18 column and eluted them and monitored in range of 200-800 nm to detect

components absorbed in visible or uv region. They investigated HPLC solvent mixture which was able to differentiate pen inks of all the seventeen sub group members as previously classified with the help of TLC methods. There are solvent mixtures of acetonitrile: water (80:20 v/v) with 0.005 M heptane sulphonic acid and 0.02% acetic acid: dichloroethane: ethanol: formamide (89:10:1 v/v), acetonitrile:tetrahydrofuran:water (924:432:644 v/v) with citric acid (1.75g/L) and hexane sulphonic acid (0.75g/L), methanol:water (60:40 v/v) with 0.005M tetra-n-butyl-ammonium phosphate at pH 7.2, methanol:ammonium acetate solution (pH 9.7) (9:1 v/v) used as eluents. They developed chromatograms for every ink running over all wavelengths in the ultraviolet and visible regions, i.e. 200 to 800 nm and used to determine peak purity by examining ultra-violet spectrum of every eluting peak of the chromatogram. The obtained UV spectrum were found to be the same throughout the chromatographic peak width if the compound was fully separated from other ink components, the peaks having same retention times in various chromatograms were compared from the achieved absorbance spectrum of the peak with that of its first and second derivatives.

Lofgren et al. (69) proved HPLC as a satisfactory technique for analysis of printing inks. Printing inks were extracted using two steps process. At first, heating of ink with dichloromethane, for few minutes and secondly re-extraction of preheated ink with 2% hydrochloric acid in methanol. The most samples were found to be satisfactorily separated adopting these two steps for extraction. Printing ink leaving any residue on the substrate was finally extracted from sample by heating again with pyridine for at least 5 minutes at 80°C necessary for only blue printing inks. Some of the blue shade of inks remained unextracted from scripts using the extraction procedure due to containing various phthalocyanines remained insoluble in solvents. They were resistant to heat but showed exclusive fastness to light. Separation of printing inks into their components was obtained using four mobile phases. Researchers observed that the best separation with well resolved peaks and a broad variation in retention times was obtained using mobile phase combining with low pH and perchlorate as ion pairing agent. They noticed that the separation efficiency was increased by using acetonitrile instead of methanol and owing to gradient elution, decreased the changes in baseline. They also explained that the eluent of (I) constituting 30% acetonitrile and 70% water with 10 mM KClO<sub>4</sub>, using perchloric acid for adjustment of pH to 3.0 and another (II) containing 100% acetonitrile in a gradient combination was proved to obtain the best separation. They used photodiode array detector to monitor column effluent at 254 nm, for excitation at 350 nm and for emission at 550 nm which employed in fluorescence detection. They determined that the results possessed excellent identification power for all the samples from these two detectors used in their method. They also concluded that the inks composition of the same shade on the same substrate was not distinguished if analyses were performed for several suspected documents.

For the identification and dating of fountain pen ink entries on paper, Wang et al. (70) adopted a new process called as ion pairing high performance liquid chromatography. Fountain pen ink of black and red colors have been discriminated by comparing the number of resolvable main or minor dye constituents and also the relative peak intensities for every component. The relative peak height for the dye components were found to be changed linearly with that of the aging time, particularly under natural conditions. The scientific evidences for fountain pen entries on suspected documents were obtained by estimating dating factors related to degradation, characteristics of dye component etc.

Kher et al. (71) were excellently separated blue ball point pen ink samples by a HPLC method using a recent technique of photodiode array detection (PDA). A classified flow chart was originated for the chromatographic data on the basis of the presence and absence of characteristic peaks at different wavelengths to differentiate qualitatively between the inks studied. The principal components analysis (PCA) was utilized to classify qualitatively for the similar data estimating resolution between one pair of class of ink samples. They noticed that the black inks samples were differentiated with satisfaction using two dimensional data presentation of the peak area and retention times at the particular wavelengths. The blue inks were differentiated by analyzing the chromatographic data at four different wavelengths simultaneously with a cross validated PCA. The results indicated that HPCL-PDA coupled with chemo metrics could make a powerful discriminating tool for the forensic chemist.

Varshney et al. (72) illustrated the use of HPLC in the ink analysis of the scripts which were typed with seven electronic type writers. The method is extremely sensitive and can be employed in the routine analysis. The resultant R<sub>f</sub> values of each resolved dye component and their visible spectrum scanned in range of 400-800 nm indicated that the similar chemical composition of inks is being used in all the six type written ribbon inks except seventh one which has completely different chemical composition with respect to others.

Gas chromatography (GC) or mass spectrometry (MS)

Gas chromatography has known limited applications in the field of ink analysis as most of ink samples have visible components, are virtually non-volatile. The volatile ink components that constitute the vehicle (73) have been analyzed for dating primarily rather than inks (74). Literature survey presents that the most widely used technique for separating and then analyzing inks is still HPLC although it needs skillful technician to

operate instruments for HPLC, a large ink sample, higher costs than the chromatographic techniques used other than HPLC. GC-MS is proved as an important technique to evaluate qualitative as well as quantitative estimation of volatile organic compounds in ink samples. Using GC-MS, the target compounds must be physically separated before detection and during detection mass spectrum of each component is obtained and target compounds are identified by determining their retention time from recorded gas chromatograph and molecular mass peaks from the obtained mass spectra. They quantitatively estimated their peak area in comparison to reference obtained from spectra. Sample preparation is to extract target compound in volatile organic forms from the sample matrix of non volatile substances in ink such as pigment etc. A conventional method liquid-liquid extraction or head space (HS) sampling may be utilized for sample extraction procedure. Sample is placed in a sample port, from here target volatile compound and gas (mobile phase) is passed through a long tubular column coated with adsorbent (stationary phase) on inner walls which placed in a heating chamber which is heated previously according to temperature-time programming and volatile target components reached partitioning equilibrium between stationary and mobile phase and finally reach detector to obtain the required results. A small amount of sample containing target compounds are needed e.g. 1 µl of 10 µg/ml solution. Solvents and additives in ink samples can be detected by extraction with an appropriate organic solvent and subsequent analysis of the extract using GC-MS (75-78). Inks have also been analyzed for the volatile component using GC (79, 80) to dating.

A recent technique for analyzing colorless compounds present in ball point pen inks, carrying out by direct thermal desorption of the ink on paper and subsequent chemical analysis of the volatile compounds by GC-MS was proposed by Bugler et al. (81). In comparison to liquid extraction the chemical analysis of extracts, the technique prevents the risks of possibility for contamination. Thermal desorption made the enrichment of volatile components and hence the sensitivity is very high. Even from old samples it is not possible to obtain chromatograms to determine binder polymers, solvents and additives by this method. Pure binders or the samples that were old enough used to manufacture inks were analyzed to produce analytical results to specific polymers leaving no doubt. To prove the practical applicability they analyzed hundred twenty one ball point pens inks, none having the similar colorant profile and grouped the pens into resin and solvent categories. Again Bugler et al. (82) derived two main approaches to determine the age of an ink, first, indirect dating based on chemical analysis of ink and subsequent comparison with known chemical in collected reference which allowed for an anachronism to be detected. Second concept is based on determining ink constituent i.e. solvent which change with age and proved an important factor for detecting age of ink on paper. So at a certain low temperature, the relative amount of solvent release and its reduction with time can be utilized to determine ink age. It was noticed that many inks appeared a significant reduction with time can be used to determine ink age. This age depending factor was studied in eighty five different inks whose age ranges from 1 week to 1.5 year. However, some of the inks showed significant decrease to this factor upto an age of numerous months and that the aging procedure can be monitored with in this period. For other ink samples, the age depending factor decrease comparatively fast. Further, Burger et al. (83) also estimated evaporation of solvent occurred by aging from ball point pen inks by GC-MS. Sample preparation was carried out with two different thermal desorption systems. The classification of thirteen inks was made regarding their solvent, polymers and additives. Aging produced variation of above mentioned compounds and can be possible to monitor forged samples either naturally or artificially.

Analyses of solvent 2-phenoxy ethoxy ethanol as minor impurity in inks by thermal desorption and GC-MS was identified by Laporte et al. (78). This impurity can be a major component in old samples of ink on paper as the evaporation rate of the impurity is much lower as compared to phenoxy ethanol itself.

Wilson et al. (79) differentiated black gel inks using chemical technique such as GC-MS. They developed a flow chart which allowed a systematic estimation of a questioned ink. Additionally, the study of volatile compounds analysis of gel inks proposed that some of the unique additives may be mixed in gel inks that are always found absent in other non ballpoint inks.

Weyermann et al. (84) innovated methods for ink dating using GC-MS based on solvent analysis and presented a wide picture for the phenomenon of the ink dating field which comprised four main articles that are – aging process, validation procedures, dating methods, and data interpretation.

Siegel (85) founded the utilization of laser desorption mass spectrometry as a valuable tool, in not only determining the structure of dye molecules constituting inks as colorants but also to track the changes take place in their chemistry, as inks and documents aged. Researcher also explored the procedures for evaluating artificially aged paper scripts under the influence of UV and visible lights.

Zhao et al. (86) simultaneously used GC and HPLC techniques for analyzing the ink of ball point pen. Sixty five different blue gel inks were analyzed using pyrolysis gas chromatography which was performed with a CZ-100 pyroprobe system having a coil filament with a quartz sample tube at 770°C for 10 sec was used to perform the pyrolysis. Gas chromatograph of Agilent-6890N make was used with Nitrogen phosphorous detector. A DM-5 Dikma Technology column (30 m x 0.32 mm x 0.25 microns) was taken to run the sample.

The gel inks were separated into three classes on the basis of the number and retention time of peaks in the programs. The most of the gel inks kept into the second class groups which showed two characteristic peaks for copper phthalocyanine pigment. The result concluded that the ratio of the peak areas and retention times obtained for components was fixed and reproducible. The age of documented blue gel ink was primarily invented by the rational change rules adopted by the scientist for main component in the ink and the curves of writing ink age on script were obtained.

Brazeau and Gaudreau (87) described the solid phase micro extraction (SPME) sampling technique, together with GC-MS for quantitative analysis of solvents in writing ink. It is non destructive method in which to avoid document destruction a sampling cell was designed which directly adsorbed the solvent onto the SPME fibre through the headspace placed above the surface of document. Analysis of ink volatiles are then desorbed into a gas chromatograph from SPME fibre in which a mass selective detector (MSD) is united i.e. GC-MSD. With the help of this method it is possible to determine the quantity of ink solvents on written scripts for a maximum period of two years.

Ng et al. (88) characterized ball point inks by electron spray ionization mass spectrometry (ESI-MS). In This method the ink from paper was extracted an aliquot of 30 µl of benzyl alcohol. The solvent extracts of ink 1 or 5 m long lines from scripts were analyzed to use direct ESI-MS analysis in positive as well as negative modes. This instrument takes only 3 minutes to complete analysis. The detection of basic and acid dyes constituting the inks are carried out in the positive and negative modes, respectively and each dye give one or two characteristic ion peaks. The recorded mass spectrum signifies mainly the composition of the dyes of the ink and it was unaffected by the paper type by which the ink extraction was done or any natural ageing process of the ink on paper in the absence of light. However, exposure of written script to fluorescent illumination caused chemical transformation in dye molecule e.g. dealkylation of polyalkylated basic dyes which resulted in changes in the homogeneous distribution of the dyes. A total forty four blue inks, twenty three black inks and ten red inks have been analyzed and their mass spectra were utilized to make a record in a library. This analytical method is simplest and fastest way by which ink samples were successfully able to compare and a rapid screening of inks must be carried out by searching online library to solve the purpose of forensic investigations of documents.

Weyermann et al. (89) exhibited liquid extraction followed by split less GC-MS in the selected ion mode to measure the quantitative decrease of solvents like ethoxy ethoxy ethanol, phenoxy ethoxy ethanol, dipropylene glycol and phenoxy ethanol and from paper script written with blue parker make ball point pen. The obtained data is allowed to draw aging curves for the pens. In this report scientists proposed that discrimination between fresh ink entries lesser than two weeks age and older scripts is possible under the conditions of storage in laboratory.

Blue ball point inks have been distinguished using laser desorption ionization mass spectrometry (LDI-MS) techniques by Weyermann (90) resolving dyes from inks and he has also compared the optical method and standard method of high performance TLC. The classification of pens has been made into twenty six classes by LDI-MS and eighteen for HPTLC method. He has proved LDI-MS technique as a more powerful tool in comparison to HPLC to differentiate ink samples because it provides advantage to determine molecular information about dye like structures, molecular weights and relative quantities of dyes by calculating peak areas at a particular retention time by running spectra and analyzing time was too short in contrast to other steps taken in HPLC like complex extraction, application and other development stages. However, using positive mode LDI-MS technique, the identification of only basic dyes and pigments were possible while additional information has also been obtained about acid dyes using HPTLC.

Sandip et al. (91) tagged ball point pen ink with varying amount of rare earth thenonyltrifluoroacetate and analyzed by inductively coupled plasma mass spectrometry ICP-MS. The satisfactory recoveries and good linear relationships of concentration against intensity were observed. This method is suitable for tagging of ballpoint inks for absolute relative age determination.

The molecular weights of various constituents in dye in inks were determined by using matrix assisted laser desorption time of flight (MALDI-TOF) and electro spray ionization (ESI) mass spectroscopic analytical methods (92). The dye constituents were resolved using TLC. They also scanned fluorescence spectra by recording them for emission over 400-700 nm and for excitation over 200-500 nm so able to characterize and identify dyes for ink dating.

Grim (93) programmed new advancement in laser desorption mass spectrometry by operating in positive and negative ion modes. He renewed the technique as a non destructive analytical process. Commercially available pigment sold as Prussian blue was used as colorant. Identification of this pigment was approved as copper phthalocyanine and green pigment which was the mixture of blue pigment and a yellow pigment and assigned as combination of Prussian blue and lead chromate.

The progressive exploration of a method using GC-MS was discussed by Papilloud and Baudraz (94) for detecting UV inks. The limit of detection represented by them can reach the order of magnitude of parts per billion (ppb). The process consist the placement of a known surface of the printed paper in contact with stimulants in totally controlled condition of contact surface, storage and temperature after the step of concentration. HPLC-Photodiode array detection (PAD) or GC-MS were used to carry out by chromatographic analysis. There must be a need to pay special attention to catalyst for photo polymerization work as photo initiators (Catalyst for photo polymerization) and to the products obtained after degradation. The quantitative estimation of traces of additives degraded products as bye products was carried out using validated method.

Reports by Jones et al. (95) mentioned the fact of the scripts possessing alteration not visible can be detected using mass spectrometry of written inks on paper with a new ion source called direct analysis in real time. Forty three different inks were examined. Both dyes and persistent but thermally labile components of the inks are analyzed by scanning their mass spectra mainly as protonated molecules (M+H)<sup>+</sup>. The obtained spectra identified some of the ink samples of calculating molecular structure of ingredients and data was collected as spectra in a searchable library, which was then challenged with spectra recorded for every ink to match. The best match for each of the challenge spectra was correct for all except one ink that was matched with a very similar ink by the same manufacturer.

#### Capillary electrophoresis (CE)

The analytical technique that is proved an important and useful tool and provide lesser time consumption for high resolution of complex mixtures is Capillary electrophoresis (CE) (96,97). The two related electrokinetic effects involved in this process are electrophoresis and electroosmosis which are performed to separate mixture components. Terabe et al. (98) introduced the use of micelles in CE to make this technique more advance to facilitate the resolution of neutral species. A capillary tube is filled with sodium dodecylsulphite (SDS) micelle solution and high voltage is applied to it, the negatively charged SDS micelles results to migrate toward the positive electrode at a velocity (V<sub>ep</sub>) by electrophoresis and the aqueous solution flow toward the negative electrode at a velocity (V<sub>eo</sub>) due to electroosmosis. The micelles move slowly toward the negative electrode because V<sub>eo</sub> is greater than V<sub>ep</sub>. When a neutral analyte is introduced into the micellar solution, a small fraction of the solubilizate may be solubilized into this micelles and then migrate inner to the micelle with the bulk flow. The analytes partitioned selectively into the micellar phase which allow them to move at different rates from the bulk at electroosmotic flow rate. The micelles are participated as the "Stationary phase," and the free bulk of solution is the "mobile phase." Micellar Electrokinetic Capillary Electrophoresis (MECE) is considered as a type of liquid-liquid partition chromatography. In conventional elution chromatography a totally retained compound is never eluted. A compound which is totally solubilized into the micellar phase is allowed to elute in MECE in a time that is equal to the effective retention time of the retarded micelles. It is the way MECE is characterized by a limited elution range. The disadvantage of CE is that it is unable to separate electrically neutral chemical compounds by conventional method but the neutral species are allowed to separate with micellar electrokinetic capillary electrophoresis (MECE). Capillary zone electrophoresis is a more stronger and powerful technique because of its additional advantages like its high efficiency, great resolution power, short time requirement in analysis so for the separation of compounds it is used with different mobility of components when a buffer is filled in capillary cartridge and a relatively high electric field is applied. More recently, capillary zone electrophoresis are invented by scientists to use for separating the dyestuffs (99-102).

In fact, the technique is very important for analyzing inks as various kinds of ink constitute materials having widely varying characteristic properties which make ink identification too difficult if adopting a single separation method to separate all the constituents as it is not suitable for a single ink containing so many additives. CE needs extra ordinary minute quantity of sample in nano liters, which preserve to be tested from much destruction. UV-Vis photodiode-array detection (190–600 nm) is used as usual to detect the resolved ink constituents. The process is automatic and very fast, and results are saved as electronic data so can be developed as a searchable reference library. The method is also applicable to dyes other than pen inks like inkjet dyes, food dyes and textile dyes. Moreover, it can also analyze non-dye ink additives such as identifiers etc. Cappillary electrophoretic techniques as compared to HPLC have not yet been applied extensively to analyze inks, despite the fact that they are suitable to separate acid and basic dye constituting inks bearing charges and also characterized by high resolving power. All kinds of pen inks as fountain pen inks (103-106), water soluble inks (107-109), ballpoint pen inks (110–112) and other gel pen inks and dyes have been analyzed successfully by CE. Blanco et al. (113) proposed CE techniques as effective, promising and economic approaches for separating a large variety of organic compounds as additives in inks and also in dyes, encountered in forensic investigations. Reliable, automated CE instruments have become commercially available and have advanced methods in the field of ink analysis.

The CE technique was compared with effectiveness and the limitations of HPLC if utilized for discriminating blue and red-pen inks (109). CE is found to be more useful than the reversed-phase HPLC to distinguish aqueous pen inks which contain ionic dyestuffs. CE using 15-mM borate buffer (pH 8.8) produce significant difference in the electropherogram for twenty two red roller ball pen and marker pen inks out of twenty six inks. To fulfill this purpose, CE of aqueous blue-pen inks containing basic dyestuffs required addition of  $\beta$ -cyclodextrin and ethanol to the carrier electrolyte.

The exact and the absolute age determination of a document by examining the ink has been a very important subject of numerous studies in the past years (114-117). The determination of date when the given document was written would therefore be a major breakthrough in forensic sciences. The use of several mechanical devices like photocopiers and laser printers etc. also increased the problems in forensic science recently (118). Because of the speed, simplicity and accessibility of photocopying, forensic experts increasingly encounter photocopies as documents to be examined.

Investigation was made by Fanali et al. (119) to identify inks using CE. High power electrophoresis equipment connected with a deuterium lamp, scanning in range 190 to 380 nm, and detector was used to perform ink analysis. The wavelength for detecting samples was kept 206 nm. For the ink separation, capillary cartridge was filled with a background electrolyte containing a mixture of 0.1 M ammonia acetate buffer solution at pH 4.5 and methanol (3:1 v/v). Near the detection electric chamber was positively charged, indicated the dyes from ink were migrating as anions. The water-soluble red and black fibre-tip pen inks were used as samples. They concluded that water soluble fibre-tip pen inks were found different from each other and successfully discriminated using this analytical method. Further, Siouffi et al. (120) performed experiments for separating the ink dyes using reversed phase thin layer chromatography (RPTLC) where dyes were extracted from the TLC plate and analysed after extracting by capillary zone electrophoresis. They concluded that this procedure was found suitable to use in ink dating.

Burkinshaw et al (121) evaluated the use of MECE for analyzing dyes and other chemical substances employed for the manufacture of dyes and many industries using them extensively. The micellar electrokinetic capillary chromatography (MECC) made possible to separate water soluble, electrically neutral dye components. And also, incorporation of a co-solvent into the buffer system water insoluble neutral dye fraction could be separated. Burkinshaw noticed that two acid dyes possessing same molecular structure and relative molecular mass could not possible to separate at all using a conventional buffer (10 mM  $\text{KH}_2\text{PO}_4$ , pH 9), but a micellar borax buffer system (10 mM  $\text{Na}_2\text{B}_4\text{O}_7$  - 40 mM SDS) successfully separated them. As working with MECE scientists found increased separation efficiency in their experiments and they believed that it is the strong indication that this technique has been accepted to be an excellent method and showed potential for the analysis of the dyes.

Water soluble inks of fountain and felt-tip pens have been analyzed by McManus et al. (108) and they obtained best results using micellar electrokinetic chromatography (MEKC) with in the presence of mixed micelles of sodium dodecyl sulphate (SDS) and Brij35. The separation was found to be reproducible and led to baseline resolution for many of the constituents. The electropherograms with distinct different patterns were obtained from inks of different brands, and the authors declared that CE is a potent and powerful tool for differentiating water-soluble writing inks of felt tip, fibre tip, plastic tip and metal tips and roller ball pens (108).

The discrimination of inkjet printing inks has been developed by Szafarska et al. (122) using a method based on MECC by which thirty ink samples were analyzed and such inks were directly extracted from paper to fulfill their requirement due to increasingly frequently counterfeiting of document printed by inkjet printers.

Whiting (123) compared the results obtained by experimentation with ball point pens using high performance liquid chromatography (HPLC) and high performance Capillary electrophoresis (HPCE). Methodology were developed for sampling of black ballpoint inks were developed to test a water 712 wisp millipore injector system for HPLC and Beckman P/ACE system 5000 for HPCE. The initial data from HPCE and HPLC consistently discriminated between the used samples of black ballpoint ink. The HPCE was found to be advantageous over HPLC due to the use of buffers rather than solvents and the lower operating costs.

Water soluble fountain pen inks were assayed by Rohde et al. (124) utilizing CE in which an advanced electrophoretic separation method was developed. The more advanced of an extraction procedure for inks directly from paper as well as the evaluation of UV visible absorbance and detection of laser induced fluorescence (LIF) for inks have been carried out by CE. Good results for separating seventeen blue and black inks of different manufacturers were obtained with 100 mM borate buffer containing 20% methanol at pH 8.0. The electropherograms of the tested ink extracts from papers found distinctly different from each other in most cases. UV-visible scans were utilized for differentiating and comparing spectra of separated primary and trace constituents of inks. The detection of fluorescense for different emission and excitation wavelengths was found to be more sensitive and causes the complications in the electropherograms due to excitation of co extracted additives of fluorescing paper.

Crystal violet (CV) was irradiated by Chun et al. (125) to obtain various N-demethyl cation products under Hg-Cd lamp for different exposure times. The photodegradation products were effectively separated by Capillary zone electrophoresis (CZE) on the basis of differences in their molecular weight. In contrast, electro kinetic chromatography (MKC) using the surfactant SDS was not found to be effective due to very close binding constant of the demethylation product and SDS for separation. As micellar electro kinetic chromatography (MEKC) analysis was able to separate neutral components from the inks hence it has its importance in forensic science. Thus, MEKC can be utilized to obtain an ink fingerprint. Since, each ink is unique as manufactured at a specific location and time. CZE is useful for dating ink because CV is the primary ink dye which photo degrades slowly.

MEKC was also applied by researchers (111) to separate dyes from black ball-point-pen inks. Analytical procedure utilized standard mixtures of dyes containing methyl violet B, Victoria blue B and solvent black 3 and sample requirements were obtained from a black ballpoint-pen ink that was extracted from paper in less than 15 minutes, yielding individual “fingerprints” of different inks so that able to recognize them. The results revealed the potential of CE in analysis of such samples and the benefits of using such a small sample size in this technique.

## **II. Luminescence**

Ink constituents has been discriminated by a technique estimating enhanced luminescence (126) in which ink ions has illuminated with green or blue light, and infrared luminescence was recorded photographically through a filter on an infrared sensitive film, only permitting to exit infrared light. The investigation involved a principle of excitation of the dye molecules to a higher energy level by the absorbing a photon and after a time period can return to the ground energy level in one or two mode. First, in which energy decay took place via thermal radiations while in other mode, the excited molecule come back to ground level after the emission of radiation. The frequency and energy of molecular collisions were lowered by decreasing the temperature. As a result the intensity of luminescence was lowered at normal temperatures so that the proportion of excited molecules was able to decay emitting radiation increases. The inks on document were made to cool using liquid nitrogen to enhance the luminescence so that ink originality on the surface was decipherable.

For differentiation of inks Sensi et al. (127) has been investigated a technique of infrared luminescence which was found to be very effective for a number of inks to differentiate dyes in them. The method is designated as nondestructive technique for examining inks and on the basis of their infrared luminescent contents, inks were classified into three groups that contain

- (1) Dye constituent that luminesce,
- (2) no luminescent dye constituents and
- (3) Constituents some luminesced and other did not.

The third class constituted of about 50 % of all ballpoint inks. All of the ink samples were difficult to differentiate using solely this nondestructive technique because inks in the third group could may now either non-luminescent or highly luminescent constituents depending upon their masking components, so may be indistinguishable from inks of the first and second groups. They concluded that examiners should take extra precautions using infrared luminescence method to discriminate among inks. Before making any assured determination, pretesting is needed to decide that both luminescent and masking components were present in suspected ink sample.

### **Micro spectrometry**

Laing et al. (128) differentiated writing inks of similar color by separating their dye stuffs using thin-layer chromatography and then recording the visible transmission or reflectance spectra of the separated constituents. They carried out studies to know the effect on analysis from different paper. The spectra were recorded by an instrument, a microspectrometer. For transmission measurements, a small disc of paper about 0.5 mm in diameter having ink depositions was punched out of the paper with a sharp hypodermic needle and put on a glass slide placing a drop of xylene-based mounting medium. The stained paper fibres with ink were separated with a scalpel blade under the microscope and then applied a cover slip on it. Visible spectra were recorded from 390 to 590 nm in reflectance and in transmission modes. The comparison of spectra were made using, differences in the number of absorbance maxima and the wavelengths at which maxima observed, and differences in the relative intensities of absorbance in spectra that showed more than one maxima. They concluded that primarily, the reflectance method found to be attractive due to the requirement of little sample preparation. However, the reproducibility of spectra scanned in the reflectance mode was poor due to bronzing i.e. the appearance of a reddish metallic sheen on the ink line. The problem of bronzing was exempted using a

mounting medium and adopting transmission mode. The results indicated that there were no significant differences between spectra that obtained from the various types of papers used.

The spectra of inks obtained by micro spectrometric technique are deviated from the Beer- Lambert law due to scattering and variations in the paper opacity in the transmission as well as the reflectance modes and also because of bronzing phenomenon in the reflection mode (129). Zeichner (130) concluded that the results are poorly reproduced even using this method if ink application was on tinted paper who attempted to make improvement in the discrimination power of microspectrophotometry for examining ink traces on paper by transferring a pinch of inked fibres on a slide and crushing it with using an engraving tool or immersing in a mounting medium. While crushing some acceptable pressure is exerted on glass slide which must bear by it to prevent breaking. They tested ten blue and ten black ballpoint pens, roller pen and fibre tip pen. The pen inks were used to mark on glass slides directly either by writing or by pressing refills on the slides. All spectra of inks were recorded by Docuspec TM/1 computerized microspectrophotometer (Nanometrics Inc.) which includes Olympus BHT microscope with quartz halogen lamps. The instrument is equipped with a variable measuring aperture having wavelength ranging from 380 to 764 nm. The influence of the paper type on the obtained spectra was studied by making comparison of recorded spectra on brown cover paper to those on a white paper. The studies indicated that all the blue and black inks tested obeyed the Beer-Lambert law and reproduce results exclusively. They observed that the spectra of crushed ink fibres were different from spectra of respective uncrushed ink deposits on glass. These differences in the spectra caused by crushing due to the pressure applied during crushing. These results were reversed when the crushed area dissolved in water and then dried and they concluded that the transmission spectra of traces of sample for inked paper film crushed on glass slide resemble with the spectra of crushed ink deposits and are more reproducible than spectra of ink fibres in a mounting medium. This is a special advantageous in the case of testing traces of ink on tinted paper.

#### **Diffuse reflectance fourier transform infrared**

The inks have been characterized by using Fourier Transform Infrared (FTIR) spectrometry (131,132). Harris (133) proved its use of diamond cell transmission and micro-reflectance spectroscopy not to be successful for analyzing paper fibres saturated with inks. Scientists believed that diffuse reflectance (DR) FTIR might be a reliable method as a nondestructive analysis for ink on paper, but Harris obtained spectra from ink on paper have not compared with known reference spectra of the known and same pure pink inks. Other nondestructive analytical attempts to analyze ballpoint ink on paper by both reflectance and diffuse reflectance utilizing FTIR microscope were also not proved successful (133). The paper showed strong absorption which tended to mask any absorption contributed by the ink. The attempts were made on FTIR microscope utilization to analyze extracted ink sample by transmission on potassium bromide (KBr) proved partially successful. The casting a film of the extracted ink sample resulted in the formation of a ring of dye constituents which tended to separate on the KBr window, and producing a different spectrum from a reference spectrum of ink of the pink color, indicated that analysis of a small portion of the dye ring would not be represented in ink sample totally.

Fuller and Griffiths (134) segregated samples by TLC followed by FTIR analysis using DR. The analyses of solids in solution using DR with FTIR have also been studied by Suzuki and Gresham (135). They observed that fine spectra could be produced from directly deposited samples of a solution onto KBr, previously packed into a micro sample cup and followed by evaporation of the solution. FTIR software has been utilized by Merrill et al. (136) to which provided a searchable spectral library to be prepared from diffusion reflectance. FTIR spectra of known samples of inks by which they may investigated dye components, resins and other additives in writing script and also extracts of ballpoint pen inks. They found that the inks from different manufacturers differentiated successfully. Because the software was able to subtract spectra, they found that it could be used beneficially to detect resins which was invisible in TLC.

Studies performed by technologists Sarin et al. (137) has indicated that Micro Reflectance absorbance FTIR (Micro RAS-FTIR) spectra of the forged color xeroxed documents could be clearly differentiated with original or forged one. The method has proved as excellent one in non destructive approaches for examining questioned color documents.

Hiroka (138) scrutinized seventy four aqueous and oil based ball point inks by four methods which were photographed before and after exposure to UV and visible light, TLC followed by densitometry, x-ray micro analysis and visible light spectrophotometry and concluded that it is possible to ascertain the brand of black ink by which entry was made in a criminal document by employing the above combination of procedures.

Wang et al. (139) classified one hundred and eight blue inks using FTIR spectroscopy into two classes on the basis of presence of main ingredients. Spectral properties of inks e.g. frequency and absorbance are described by way of artificial intelligence of pattern recognition and thirty five subgroups distinguished by their correlation coefficient ( $\lambda$ ). Under heat or exposure to UV light a mode of change in the age of inks has been obtained.

Awab et al. (140) made interpretations from FTIR techniques for forensic discrimination of marker pen inks and utilized Swab Method using cotton buds to collect sample and then recorded IR spectra using attenuated transmitted reflectance (ATR) spectroscopic technique. They concluded that non permanent inks have weak amine bands at 823-850  $\text{cm}^{-1}$  with emphasized dissimilarity between permanent and non permanent ink at 2345 and 2361  $\text{cm}^{-1}$  attributed to the  $\text{C}\equiv\text{C}$  vibrations, 1736 and 1737  $\text{cm}^{-1}$  corresponding to  $\text{C}=\text{O}$  stretching and 1204  $\text{cm}^{-1}$  to  $\text{C}-\text{O}$  bending.

Feasible investigations of micro attenuated total reflectance (ATR) FTIR spectroscopy to characterize seal inks has been made by Dirwono et al. (141) and concluded that the method can identify origin of the red seal inks with accuracy.

Zaharullil and Kalthom (142) scanned FTIR spectra in the range 450  $\text{cm}^{-1}$  – 4000  $\text{cm}^{-1}$  and also UV-Visible spectra in the wavelength range 400 nm- 700 nm to discriminate ballpoint pen inks which were primarily extracted in methanol from paper.

### **Luminescence photography**

Kirchner (143) inferred for ink identification by combination of the techniques such as thin-layer chromatography followed by luminescence photography which has been accepted as a very sensitive method for determining components obtained from thin-layer chromatography. In this project, above than a hundred different ink samples were collected and resolved their components by thin-layer chromatography using a variety of solvent system as elluent either used previously by scientists in their studies or modified by other investigators (144,145) and which lead to a more reliable resolution of the ink dyes. For ballpoint pen inks, an elluent of acetone and distilled water (85:15 v/v) for black inks and absolute ethyl alcohol, 0.88 ammonia water solution (99:1 v/v) was used to obtain best results.

In order to identify and distinguish different inks, Laporte et al. (146) separated ink samples using TLC and evaluated for comparison utilizing optical examinations. 100 pens were randomly obtained from a variety of sources and their respective ink compositions were compared with standard.

### **Laser excitation and spectroscopy**

Sinor et al. (147) made use of lasers and optical spectroscopy for examining questioned documents and distinguished inks visually via laser-induced fluorescence. In such circumstances, photographic documentation of the case suffices and none is required to contemplate spectroscopic measurements. They are, however, primarily concerned with instances in which similar inks were not discriminated by visual inspection even under laser excitation. Three techniques used are absorption microspectrometry, thin layer chromatography and infrared luminescence. Thirty ballpoint pen and porous tip pens with black, blue and red color inks were investigated by Sinor and coworkers. Absorption spectra were run by using a Perkin-Elmer 356 spectrometer as an instrument. IR luminescence photographs of traces sample were recorded using 5145 An Ar-laser excitation. The thin layer chromatography was carried out by using 100 % C-18 silanized silicagel glass plate. A mixture of equal parts by volume of acetone, methanol and distilled water was used as an elluent for separation. Ink samples were applied by spotting. It has been observed from their results that the studies for separation of dyes on TLC plates using laser excitation could substantially improve sensitivity and also demonstrated that luminescence efficiency was increased by reducing the sample temperature using liquid  $\text{N}_2$ . They also found that ballpoint inks tended to be suspensions, rather than true solution, anticipated small fluctuations of composition for a given sample. Accordingly, minor spectral differences should not be considered as a basis to conclude ink differences.

Cantu et al. (148) recorded spectra for luminescence and observed the inks after dye separation by TLC. They suggested the use of an energy source to illuminate the separated dyes named as Argon ion laser. IR sensitive camera system was used to record all the results which are provided with a silicon-viticon IR-sensitive cathode ray tube (CRT) in its heart and a fluorescence spectrophotometer is also attached. They concluded that the excitation or emission spectra of an ink known to exhibit IR luminescence predicted what the behavior of ink was when observed with the different viewing systems. Their work showed that the different observational recording system on the same ink did not produce independent results but were part of the same fluorescence emission.

### **Raman spectroscopy**

Fabińska and Trzcinska (149) appraised ball point and liquid inks using four methods to identify and to differentiate inks – observation of TLC under visible and IR light, in conjugation with IR spectroscopy and MK-FTIR and an advanced method Raman spectroscopy was also used. It was found that Raman spectroscopy method could serve as a supplement to the optical method, however, the destructive methods cannot be completely disregarded.

Geiman et al. (150) enhanced applicability of Raman spectroscopy and surface enhanced Raman scattering (SERS) in the analysis of synthetic dyes in ball point inks and was also investigated a comparative study. They used a dispersive system (633 nm, 785 nm lasers) and a FT system (1064 nm laser) to obtain spectra of ten dyes under different analytical conditions such as powdered pigments, solutions, TLC spots while high fluorescent background and poor spectral quality has been often characterized the normal Raman spectra of studied dyes. SERS were proved to be generally helpful. A single ball point ink and its dye standards were also developed on a TLC plate thus demonstrating a visible forensic application for the technique.

Kunicki (151) also evaluated discriminating power of various methods using, ball point pen inks including optical methods, Raman spectroscopy and TLC methods. An essential element of his evaluation was finding appropriate extracting solvent and developing solvent systems that would ensure production of a well differentiated chromatogram.

### **Other techniques**

Morsy et al. (152) obtained ink identification from non distractive methods such as filtered light examination (FLE) and microspertrometry (MSP) were compared with that obtained from Raman spectroscopy and surface enhanced Resonance Raman Scattering (SERRS). The TLC and X-ray analysis have also been carried out and concluded that not a single method can identify all types of inks. Each method has its own advantage and importance to distinguish ink samples.

Ramotowski and Regen (153) initialized studies on archived materials, affected by the electron beam irradiation on archived materials, some of the data available on the effect that this phenomenon would have on forensic evidence for different types of writing inks including ball point, gel, felt tip and roller ball, were brought to standard mail irradiation conditions. A thin layer chromatography analysis and video spectral comparator were used to determine both the control and the irradiated samples. Some of the polished studies noticed changes in the presence or absence of color bands for dye in the chromatograms for irradiated writing inks. Some other similar studies reported the formation of some additional dye bands on the resulted chromatogram while lots of report missing dye bands. Although, using standard methodology, testing guidelines and techniques none of the 97 irradiated ink tested were noted to exhibit any significant optical or chemical differentiations from the control samples. Additionally random testing for some of the writing ink samples with another solvent system used, did not give any changes. Therefore, one control ink did produce some minor changes in optical properties and characteristics of dye while the irradiated sample remained stable. Significant changes in the ultraviolet florescence characteristics of irradiated samples of paper itself without ink were also observed in results.

Magarelli et al. (154) characterized sepia inks. Sepia inks contain bio pigment melanin. None method allow to determine melanin due to its intrinsic chemical properties as they are insoluble in broad range of solvents and pH as well as difficult to purify as a result of heterogeneity in their structural features. They purified sepia melanin according to an undescribed method. Extraction and purification was carried out using HCl (0.5 – 3.0 M) treatment under mechanical or ultrasonic agitation. Purified melanin was obtained and characterized using elemental analysis (EA), UV-Visible and IR spectroscopy and inductivity coupled plasma mass spectrometry (ICP-MS) for metal ion analysis. Finally quantitative studies of chemical degradation of Eu polymers to pyrrole 2, 3, 5 – tri carboxylic acid and pyrrole – 2, 3 its carboxylic acid by HPLC were performed. They developed such a method that can be used to get sepia melanin with a considerably less cost which could prove very valuable as an important standard, in future, for determining eumelanin and pheomelanin as well as in a wide field of scientific and industrial applications such as human and veterinary medicine, pharmacy and cosmetics etc.

### **III. Conclusion**

In the past, different research initiatives have performed to characterize and to age inks by analyzing their ingredients either dyes or other constituents. Analysis of different inks is useful in forensic agencies as the hand written, Xerox and printed paper or other substrate surfaces with ink remains widely used and trusted for any business and legal documents and the problem of forgery is of great interest in forensic science. The analytical techniques are utilizing to overcome such problems in which the documents used in criminal activities or in course of civil litigation either altered or created specifically for the purpose of deception. On the other hand, these are utilized by ink manufacturers for the formulation of better quality of ink. Ink analysis is also helpful to classify different inks as classification can play an important role to make a library of analytical data of so many kinds of inks.

Besides these, dyes and components are characterized through ink analysis, may be utilized in dying and painting of automobiles, hair, clothing, walls, decorative pieces and other so many articles in our daily life, sometimes become a part of criminal activities e.g. in case of automobile- hit and run is most common. Hence, identification of these have its excessive application in forensic science. Also, many ink gradients especially

dyes have their pharmaceutical importance and their characterization is also beneficial in pharmacological and biomedical purposes.

Despite the importance of existing work done, future research should include-

- quick analysis of different ink samples isolated from different grade papers or substrates,
- achieve more and more exact information about their composition,
- reproducibility of results to determine reliability of each technique,
- estimating the precise date of documentation by fast and straightforward method,
- identifying the source of written, typed, printed and xeroxed documentation.

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