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A Review on Ink Examination Using Chromatographic Techniques

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ABSTRACT

Forensic document examination evolves to be remarkable subject of discussion for research. Experts working in the field has to be pragmatic in forming an opinion apart from tracing out the authenticity of a document so as to impart justice in the court of law. ink analysis in addition to handwriting features play a significant role in determining the source, authenticity and dating of documents. Chromatography is one of the widely used technique for various forensic evidence since decades. The present article focuses on use of chromatographic techniques for analysis of ink. The article will help examiners understand the relevance of chromatographic technique and choose the technique appropriately.

Keywords*: Questioned document, ink examination, forgery, chromatography*.

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INTRODUCTION

The word ink has been derived from Latin word "encaustum", a name given to the purplish red ink used by Roman Emperors to sign their orders. The literal meaning of this word is 'burnt ink'. The first use of ink has been dated as early as 2500 B.C. by Egyptians. They used a mixture of lampblack and glue for writing 'Old papyri'. They even added certain preservatives to prevent decomposition of ink. They also used gums and glues as a bonding agent.Later, between 2697 B.C. and 2597 B.C., China ink or India ink came in existence. The soot obtained from the burning of pines and oil in the primitive lamps was utilized by Chinese for preparation of ink. Musk was usually added to modify the odor of oil. These inks were stored in the form of cakes or sticks [1].

While using, these cakes were shaved and mixed with water. These inks were also known as India ink as the raw material used for manufacturing came from India. This ink was also called carbon ink. These inks were very fixed and did not decompose by moisture, air, light or microbial activity [2].

Chinese also used natural plants dyes and minerals with water as ink. Similar method of production was used by Hebrews and Arabians for developing ink. Dioscorides in between 40-30 B.C. discussed the proportion of lampblack and oil to be used during manufacture of ink in his dissertation on medicinal erbs [3].

This art of manufacturing ink lost between the civilization of Egypt and Rome. The Romans did not use any manufacture ink for writing infect they used rich brown excretion of cuttle fish for writing. The manufacturing of chemically made ink again became popularized in around 200 A.D(Pines, 1931). Gradual development of ink between tenth and twelfth century led to transition from carbon inks to iron gallotannate inks. These iron gall inks are still used with certain modifications as blue and black writing inks. This variety of ink came into existence comparatively early in Ancient Syria due to easy availability of important raw materials, the gall nuts and iron sulphate [3]. The earliest reference of iron tannin ink has been found to be of monk Theophilus who describe a method of manufacturing writing ink from thorn wood. Thorn wood is a tannin bearing bark. According to the description, and aqueous extract of wood was evaporated to dryness and the powder obtained was mixed with iron sulphate also known as green vitriol [22. Anterior Orient is considered to be inventor of gall ink which is derived from Oak species. According to the data available, it gall-wasps deposited its ova on oak species which developed into galls. Philo by Byzantium (2nd Century AD) and Martianus Capella (5th Century AD) described the utilization of galls for manufacturing of ink [4].

The work on iron gall inks progressed and later during mid to late 1880s, ink classification proved to be a huge commercial success. Due to its commercial success, ink chemists starting developing different coloring substances. Various substances such as indigo, madder, logwood and other dyeing components were used for imparting color to the ink. Gradually, soluble anilines were used as dyeing material in inks. Nigrosine became extremely popular coloring agents due to its blueish color. Vanadium also became

popular. These ingredients were used in a popular ink instrument called fountain pen [5]. Gradual development of ink and writing instruments, led to development of ballpoint inks and gel inks [6-9].

HISTORY OF INK EXAMINATION

Since the inception of the discipline of questioned documents analysis, examiners have always been keen to search for better and more effective ways of examination. Traditional methods of analysis involved watermark identification, typewritten documents, obliterated and indented handwriting etc. Around 1950, document examiners gradually started experimentations with ink examination. Various researches started experimenting multiple techniques for analysis of ink. Initially, thin layer chromatography was suggested for identification of ink [13].

Gradually, Somerford, [22] assist paper chromatography for differentiation of fluid in. The work done till 1952 depicted that the examination of ink can be successfully conducted even with micro quantities. The market availability of ball point pen ink increased by 1952. This increase lead to experimentation of ball point inks [22]. Later, Brown and Kirk [1] compared paper chromatography with electrophoresis and reported that electrophoresis is a better technique than paper chromatography for separation of various components of ink. Various other researcher conducted studies and reported the relative effectiveness of electrophoresis over paper chromatography. [3].

In 1961, researchers suggested a chemical spot testing procedure which was effective in differentiating between specific dye constituents present in ball point inks. Subsequently, more techniques that can be used for ink examination were being explored. The studies conducted by Dick, Godown and Von Bremen regarding use of dichroic filters, IR luminescene and ultraviolet photography also contributed effectively to the field of ink analysis [5]. Further, Nakamura and Shimoda (1965) used microscopic slides as TLC plates for ink analysis thereby reducing the cost of analysis to micro scale. According to their study, they used a solvent system of ethanol, water, and n-butanol (50: 10:15 parts, respectively). The solvent system proved to be effective for separating methyl violet into 04 different spots which denoted the different isomers of pararosaniline. Subsequently, Tholl in 1966 used thin layer chromatography for partition of dyes and other components of inks. According to various studies, it was concluded that thin layer chromatography proved to be well suited for analysis of small quantities of ball point ink. Ink examination was limited to chromatographic techniques till 1966. Gradually, researchers became more interested in exploring other techniques for ink examination as well as to establish the age of ink. The dating of inks was confined to determination of phases of time when significant alterations were made in the composition of ink like change in solvent of ball point pen ink [17-20].

The earliest study for determination of age of ink was conducted by Werner Hofmanof Zurich, Switzerland. Hoffman collected ball-pen ink standards from various manufacturers. These standards were compared with ink on questioned documents; the questioned inks were dated by referring to the first production dates of the specific matching standard formulations. The study involved use of paper chromatography and TLC with various solvent systems; the usual non-destructive tests, spot tests, and spectrophotometry to aid in the examination and comparison questioned inks and standards. Gradually, since mid-1960s, the need for advanced techniques for ink examination and dating of ink increased [4]. With advancement in technology, Gorziza*et.al.* (2019) provided the characterization of ballpoint ink & dating by a broad systematic review of the studies using static and dynamic methods in the last 10 years. Identification of the composition of ink and its characterization with the reference data is the base for static method. Because of many environmental factors like humidity & light, the process & alterations which involves during the study of ink is studied in Dynamic method.Good accuracy is offered by the ink dating approaches which is concluded by them. But more research has to be done to evaluate the condition of document storage, variation in the ink quantity in pen brands, paper type & writing fists [21-24].

Chromatographic techniques used for ink examination

Zlotnick & Smith[36] reported that the significance of chromatographic techniques for examination of inks could be traced back since the early 1950s, as the compositional information bearing for their application primarily towards investigating on fraudulence, counterfeiting, forgery and other crimes.

Thin layer Chromatography

Tebbett et.al. did chromatographic study of inks for applying in forensic science. To establish the ink age, the changes in the ink composition is measured using TLC and HPLC [25]. Later, Trzcinska (2001) reported the application of Thin-layer chromatography (TLC). From the author's assessment, the chromatographic technique was regarded as the easiest, simplest as well as its resolution also was widely been used in which there exists two phases. First phase could be stated as stationary phase, this represents the layer comprise of powdered solid materials that is adsorbed to aluminium surface plane, plastic plate. These case are then kept as spots with a line drawn 1 cm over plate's bottom and was

vertically kept either with pure solvent/ solvents mixture regarded as mobile phase which runs upward over stationary phase to the plate under a remarkable height. This mobile phase tend to move up, thereby facilitating sample migration that is kept at original line. Over a certain time period, the plate was dried, removed, and further then noticed via visible light/ UV light.[26].

Tsutsumi &Ohga [27] reported that when there exists one/ more spots with a characteristic coloration, which might be witnessed/ sometimes spots developed for visualization via spraying compounds comprising of chromatogenic reagent for examining the chemical changes exhibiting different retardation factor (Rf) values. Rf could be otherwise explained as "ratio of the actual distance travelled via separated compound over the actual distance travelled by solvent front from its original drawn line indicating sample spot". Besides, Rf values provide the qualitative estimation for compounds as well as for quantitative estimation via measuring density pertaining to separated spot for the compound [27]. In addition to previous work, Kuranz (1986) carried out a renewed approach that aided in better separations of the dye stuffs exhibiting identical Rf values that are not being previously being separated completely. In order for achieving this, the author removed cellulose layers / silica gel from underlying plate carefully and then rendered various outcome than the previously achieved outcome, as the whole of eluent travelled via sample spot and thereby giving series of discrete bands over the region of overlapped bands(Kuranz, 1986).

Verma et.al. utilized a TLC approach for assessing the fibre tipped pen inks. The procedure involved with 12 signed inks of three different brands and was then subjected to examination via silica gel plate from where the ink samples were determined after ethanol dissolving. The approach utilized two different solvent approach, first involves a mixture of butan-1-ol:aceticacid:water (6:1:2 v/v), and another butan-1-ol:acetic acid:water:1,4-doxane (6:2:2:1 v/v).The samples of ink were successfully discriminated & compared by the resolved components on the TLC platesas the Rf of ink values were calculated and all the ink were characterized with the help of the above two solvent systems.After separating their constituents by TLC, these inks were identified with the help of valuable information provided by colours fluoresced in the shades of crimson, pink, orange & red as a result of ultraviolet radiation the inks [29].

Apart from TLC, Inks can be evaluated using TLC compatible devices, including video scanners, CCDs, and spectrophotometers. The inks were then hydrolysed by chromatograms and formed from a soluble compound of methanol-ethyl: ethanol: water (v / v-14: 7: 6) and acetic acid derivative (v / v-14: 7: 6) as in normal TLC. Furthermore, the adjunct instrument employed for discrimination of resolved spots over TLC plates. The specificity of colour followed by resolution comprises two factors, evaluated by authors. From the study, the author noticed these scanners were unable to sufficiently resolve constituents when the scan time was small, however could be increased via increasing densitometry scan time was further then showed since the accepted technique for examining the different colored constituents was made possible. [15].

Experiments were carried out to characterize & compare the ink using TLC by solving writing ink samples from ballpoint pens.Using the surrounding light, evaluation is done on the chromatographic profiles which are developed on a TLC plate. Using filtered light, observations are made on the similar or different formulation of ink which appears to be indistinguishable. Various illuminations of ink characteristics is shown by it but not readily. The characteristic wavelengths of radiation may be responded by few components in the mixture of writing inks which may not be visible to eyes. Definitive discrimination is proved to be effective by further evaluation which is done assist other light source along with the proper filter. (Houlgrave et al., 2011).

Furthermore, Saini *et al,* (2018) using a high-performance thin-layer chromatography each sample was completely separated. The efficiency of gas chromatographic separation by mass spectrometry of black and red ballpoint pen inks was 63.58% and 32.85%, respectively. There are two standards for regulating inks, and they are the result of primary separation and division. In the primary class, large areas of ink are separated. In the subsequent differentiation, small parts of the ink are separated [(Saini & Rathore, 2018).

HPLC

Whith &Weals (1984) announced the true mechanism of HPLC concern. Like TLC, heterogeneity can be a fluid with clumps of fluids with a high-performance fluid chromosome (HPLC) passing through a region under applied voltage using a pump. A static mesh is equipped with a piece of reinforced steel/glass tube composed of silica particles that can reach micrometres of uniform or irregular circular shape. The eleventh has been passed through a partition and ultimately verified by an identifier that identifies the isolated partitions through which it has passed. The main advantage/advantage of using HPLC is its similarity to the various complex assemblies on the surface of silica particles, which allows the tools associated with the LC subset to be evaluated. It is also observed that the liquids polarity employed in the case of mobile phase appeared to widely different from the liquid that was subjected as the stationary phase for the investigation [31].

A novel approach employed by Liu et al. [14] for pondering false entries over documents that are written with black gel pen illustrated in terms of classification followed by dating. This technique was primarily on the basis of ion pairing HPLC. This study divided 93 black gel pens under two varieties- pigment &dye based on the results basis achieved from preliminary solubility test. This ion section reagent called tetra butyl ammonium bromide (40 m mol/L) employed for separation of dye constituents. Classification of dye parts were on the basis of its number as well as from chromatographic retention times for main dye constituent. This changes with regards to dye components' chemical composition which constituted of entries of black gel pen ink on the substrate were analysed from light as well as natural aging circumstances and further was noticed from the decomposition of dye constituents and the extent of decomposition. The extent of decomposition is directly related with measurement of its aging [14].

For characterization of writing inks, Tapplet et al., (1983) developed and used a high-performance thin-film chromosome (HPTLC) for mixed ink imaging. Sheets of Merck silica gel were first dried at 60 ° C for 1 h, and weakened wells were set to 1: 5 (volume/tail) on DLC plates before using inks. If ink tests were conducted, the creators looked for experiments to determine the best soluble composition resulting from automatic colour separation by repeated chromatograms. Iso-Butanol: Ethanol: About 100% Acid: The solubility of distilled water (20: 5: 5: 10 V / V) Inks for ballpoint pens are also evaluated according to the properties related to HPTLC and TLC. It was concluded that the HPTLC was comparatively effective than TLC, as they aid in rapid development of chromatograms. It is followed by better resolution of components & small quantity of sample with greater reproducibility and increased sensitivity [23].

In case of identification &dating of entries for fountain pen ink on paper, Wang et al. (2008) said newer approach defined as "ion pairing high performance liquid chromatography". The red and black highlighter inks were separated by examining the size of the soluble primary / secondary colour components and the relative peak strength of each component. Due to the areas of colour, this comparative peak changed directly during ripening, especially compared to their natural conditions. The dating factors which are in relation with degradation, dye component & their characteristics are estimated to get the scientific evidences from entries of fountain pen from suspected documents [32].

Photodiode array detection (PDA) was used to obtain blue pen ink samples using the HPLC method. To qualitatively separate the inks, a unique flowchart has been launched. Chromatographic data were provided based on the presence and absence of brand peaks at different frequencies. Comparable quality data was collected using Primary Component Analysis (PCA) for target assessment on a range of ink sample classes. The black ink samples were separated using a 2D data display and peak retention times at certain frequencies. The chromatographic data is analyzed at 4 different frequencies with the PCA checked, and the blue ink is separated. The amazing physical separator was developed by HPCL-PDA, which is confirmed by the results combined with chemical measurements [14].

Varshney et al.examined the utilityof HPLC in the ink analysis of the scripts. These scripts are typed with 7 electronic type writers. This procedure can be employed in the regular analysis and it isvery sensitive. It is known that the same chemical composition of inks is assist in all the 6 type written ribbon inks except the last one. This determination is made by examining the RF values of each standard colour particle and their apparent range in the range 400 to 800 nm [30].

Gas chromatography (GC) or mass spectrometry (MS)

In the field of ink analysis, Gas chromatography has only limited applications.It is because of the virtually non-volatile nature of the visible components of ink samples. To determine the inks dating, examine was done to volatile ink components that constitute the vehicle. For sample extraction procedure, head space (HS) sampling or liquid-liquid extraction can be used which are the conventional methods(Stewart, 1985). The sample is placed in the sampling port, where the mixture and the unexpected target gas are passed through a long cylindrical section covered with an absorbent material (fixed phase), which is then placed in a heated chamber. Depending on the temperature, programming time and unstable target segments arrived, the balancing segment between the static and multipurpose positions and finally the detector succeeded in achieving the desired results. A sample with target compounds requires a small measurement, e.g. 1 g for 10 g / ml. additives and Solvents in ink samples can be detected by soluble normal solution extraction and GC-MS concentration analysis.

Bugler et al. [5] analysed a new process for volatile compounds chemical analysis and heat absorption directly on the paper to study soft compounds present in ballpoint pen ink [4]. In another study, Bugler et al. derived 2major approaches for determining the actual age for an ink. First approach is the indirect dating on the basis of chemical analysis from ink.Next approach is the subsequent comparison to its known chemical which is collected as a reference which facilitated for detecting anachronism. Second approach involves with determination of ink constituent which is the solvent that changes with theage. This proves as a pertinent factor in detection of ink's age on a paper [20, 28]. So, for determination of ink age,the relative degree of solvent release followed by their reduction with time could be utilized under a

certain low temperature. It was also observed that among several inks, it could be examined that there lies a significant reduction of actual time required for examination of ink age [4].
Moreover, Bugler et al. soluble dispersion is mainly the result of the maturation of inks to the detriment of the ballpoint pen, and GC-MS determined it. The model was ready and then finished with two unique heat-absorbing system. This set of 13 inks is related to materials such as soluble, additives, polymers, and various compounds mentioned above, which can be used to separate naturally or artificially refined samples [6]. Further, Wilson et al. employed chemical technique GC-MS to differentiate the black gel inks. The author devised a flow chart that facilitated for systematic estimation over the questioned ink. In addition to that, the research pertaining to the analysis of volatile compounds on gel inks suggested some of its special additives which might be added with the gel inks which were always seen absent with respect to other non-ballpoint inks [31].
Weyermann et al. [32] developed techniques pertaining to dating of ink with respect to GC-MS based solvent analysis &then gave a better perspective concerning with the working phenomenon on ink dating field which involved 4major articles. They are aging process, data interpretation, and validation procedures & dating method [32]. Siegel (2005) introduced that the laser desorption mass spectrometry's utilizationcould serve as valuable tool, which not only determines structural attributes of dye molecules comprising of inks serving as colorants, however also it could aid for tracking the changes that are taking place in its chemistry, since both inks as well as documents are aged. Also the author explored procedures that involves with evaluation of artificially aged paper scripts via UV &visible lights [22].
Zhao et al. [35] used HPLC and GC procedure at the same time to analyse the ball point pen's ink. Withpyrolysis gas chromatography, 65 different blue gel inks were analysed. It is done using a thermal probe frame coated with CZ-100 fiber with a quartz test tube at a temperature of 770 ° C for 10 seconds. The nitrogen-phosphorus identifier was used in conjunction with the gas chromosome produced by Agilent-6890N. As an illustration, part of the DM-5 Dilemma technology (30m × 0.32mm × 0.25m) was taken [35].
In addition, Blue spherical inks were identified by ionization laser absorption mass spectrometry (LTI-MS) techniques, developed by Weyermann [33], which included precipitation dyes from inks. This unique feature of the pens is offered in 26 classes with LDI-MS and 18 classes with HPTLC technology. In conjunction with HPLC in the ink testing section, the use of LDI-MS technology has proven to be a very viable and surprising asset that can be a well-integrated thorough examination. . The main reason for this is that some formulas and pigments and extra fillers have good advantages over the comparative conditions to verify atomic data and colour properties. It is achieved by exploring the peaks at a specific maintenance time while Spectra is running, and this is achieved by dividing the time, which was much less when using different and different complex extraction methods like other improvements. However, it is expected that only characteristic evidence of the base dyes will be possible when the LDI-MS process is used in the positive mode, while additional data on the presence of erosive dyes for the ink is needed when the LDI-MS process is used in the positive mode in the use of HPTLC.
Maind et al. [16] the ballpoint pen ink should be dry nonspecific nonyltrifluoroacetonate based on measurements of abnormal soil variability, and then separated by induction plasma mass spectrometry (ICP-MS). Good recoveries after significant direct binding were analysed according to their concentration and strength. This method is more reasonable if there is a phenomenon of dry marking in determining the apparent relative age. Atomic charges are also the basis of various components of colourless inks embedded in stone using MALDI-TOF in conjunction with ESI and mass spectroscopic methods. In addition, components accessible from 0 million colour components have been normalized via TLC. Explore the fluorescence spectrum by recording emissions in the 400-700nm range and excitation losses between 200-500nm, so colour hunting was an option for imaging and dating Ink.
Grim (2003) Laser absorption caused another breakthrough in mass spectrometry by working under specific and passive particle systems. The creator of this procedure has reloaded the scientific and indestructible method of ink evaluation. It includes the use of dyes - using economically accessible Prussian blue. The dye was recognized and improved by combining copper phthalocyanine and blue dye, followed by a yellow dye for Prussian blue and lead chromate [8].
Papilloud and Baudraz [18] investigated on a much more progressive method with respect to GC-MS via detecting UV based inks. The restriction for detection was represented by the investigators and it could be reach order of magnitude in units of parts per billion (ppb). This process involves with placement of known surface of printed paper which is under the contact with stimulants that is totally subjected under the controlled condition on storage, contact surface & temperature after concentration step. HPLC-Photodiode array detection (PAD)/ GC-MS was employed for chromatographic analysis. It Covers abilities such as photo polymerization reaction, photoionization (catalyst used in photo polymerization) and post-

corruption products. This quantity assessment was carried out based on acceptable specifications for damaged products, where the results were further returned in a fair / approved manner [28].
Lee *et.al.* [12] determined that use of Ultra-performance liquid chromatography (UPLC) is far better than high performance liquid chromatography in context of speed of analysis as well as sensitivity. UPLC was used for examination of 12 different types of red ball point pen inks. 144 chromatograms were obtained from which it was interpreted that discriminating power of this techniques is 95.45%.

CONCLUSION

Determining the most effective and appropriate technique for examination of overlapped inks is a challenging task. During the investigation of fraudulent documents, the composition of ink used can play a vital role in providing relevant and leading information. Many conventional techniques present in the domain of Forensic Questioned Document can be used to decipher the alterations and determine the composition of overlapped inks. However, even being a destructive technique, chromatography has proved to be one of the most preferred technique for examination of ink. Nonetheless, a novel revolution is strongly required to surpass destructive techniques with semi-destructive and/or non-destructive techniques.

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