International Journal of Medical Toxicology & Legal Medicine
e-ISSN: 0974-4614
p-ISSN: 0972-0448

Volume 27, No. 1, 2024
DOI: https://doi.org/10.52710/ijmtlm.7

Article Submitted: 20-02-2024; Revised: 24-04-2024; Accepted: 01-05-2024

A Systematic Review for Dating Analysis of Different Pen Inks using Advanced Analytical Techniques

Mukul Kumar[1], Das Anamika[2], Suneet Kumar[3] and Mayuri kumari[4]

[1,4] Department of Forensic Science, Galgotias University, Greater Noida, India -201310

[2] Department of Forensic Science, Sharda University, Greater Noida, India -201310

[3]Scientific Officer, Forensic Science Laboratory, Moradabad, India -244001

[*]Corresponding Author

Das Anamika

Assistant Professor, Department of Forensic Science,

Sharda School of Allied Health Sciences (SSAHS),

Sharda University, Greater Noida, 201310, India

Email: das.anamika@sharda.ac.in

Abstract

The forensic analysis of ink dating is a crucial aspect of document examination. It involves the chemical and physical analysis of inks to determine their age and origin. Advanced analytical techniques such as chromatography, mass spectrometry, and microscopy have been used for ink dating analysis. This systematic review aims to summarise and evaluate the recent literature on analyzing different pen inks using advanced analytical techniques. The review covers studies from the last decade and highlights the advantages and limitations of the other analytical methods used for ink dating. The review also discusses the factors that can affect ink aging and emphasizes the importance of considering different factors while performing ink dating analysis. In conclusion, the systematic review provides a comprehensive analysis of the recent literature on ink dating and highlights the potential of advanced analytical techniques in forensic ink dating analysis. This review will be helpful for forensic document examiners, forensic researchers, and other professionals involved in ink dating analysis.

Keywords: analytical, chromatography, spectrometry, dating, document

1. Introduction

Forensic examiners of documents are often presented with complex issues that must be resolved to advance investigations and legal proceedings, requiring in-depth knowledge and expertise. One such issue pertains to determining ink age, which involves evaluating the probable time when the ink was applied to the paper. This process can be challenging due to the wide range of writing inks available, the intricate chemical reactions that occur over time after ink deposition, and external factors such as storage conditions, light, temperature, humidity, etc. [1].

Analyzing ink dating can be helpful in some instances; however, it is still challenging for forensic scientists due to various factors affecting the analysis [1-3]. When examining a document's date, the process will involve a chemical, physical, and optical examination of the paper and ink used. This review will only focus on the different techniques used in ink analysis. Writing instruments can be divided into water-based (non-ballpoint pen) and oil-based ink (ballpoint pen). Oil-based ink contains vehicles, dyes, resins, and additives [1,4]. Dyes determine the ink's color, whereas vehicle-based ink contains cleaned ink compounds. On the other hand, the resins provide the ink with viscosity, adherence to paper, lubricant properties, and durability. Additives are compounds that possess specific characteristics that enhance the performance of ink. Two primary methods for ballpoint pen ink dating are static and dynamic. The static method involves identifying or characterizing the ink composition, often comparing it to other known pen ink sources. The dynamic analysis method involves monitoring ink behavior over time in response to environmental factors such as humidity and

light. On the other hand, the static approach relies on identifying inks with a known manufacturing history through visual, microscopic, and chemical techniques. The identified ink is then compared to the ink in question. For the static approach to be practical, standard reference ink specimens must be traceable and have known manufacturer information and the first production date. The static approach assumes that the measured ink profiles have remained constant over time, so the comparison standards must be stable and representative. Using more extensive and comprehensive ink collection sets can lead to greater accuracy in dating estimations, and the ink dating uncertainty can be reduced by using vastly informative and distinguishing analytical techniques for examination.

The ink age can be determined using various approaches, such as the static, relative, and absolute age approaches. Examining the ink, paper, and environmental factors can aid in determining the document's approximate age. Determining the absolute age of a document relies more on identifying the ink used rather than comparing it to other factors. Certain ink manufacturers add markers to their products, but not all inks have them because of cost limitations. Currently, no database is dedicated explicitly to these ink tags or markers. Studies have been conducted on dating iron gallotannate inks, widespread from 1920 to 1972. Before 2000, there was also considerable study into determining the age of ballpoint pens [5].

During the 1960s, an author established the world's first ink reference collection, where they examined ink profiles using ultraviolet fluorescence, near-infrared reflectance, luminescence, and thin-layer chromatography (TLC). In the early 1970s, another author created one of the most extensive international writing ink libraries, initially developed at ATF and later maintained by the United States Secret Service (USSS). They characterized the inks through semi-quantitative TLC, HPLC, FTIR, and GC. In 2009, Neumann and co-workers developed an automated method that uses mathematical algorithms, high-performance thin-layer liquid chromatography (HPTLC), and automated software to search and detect writing inks [7-10].

Different studies have explored techniques for estimating the duration of pen ink on paper in dynamic profiles. These methods involve using fading dyes that lose color when exposed to light. A straightforward comparison can be made by comparing the dyes inside the pen cartridge or recent writing to those on the paper that have undergone photodegradation. Additionally, the solvents in ink evaporate during the writing process, which differs from inside the pen cartridge. Further, the solubility of ink on paper reduces over time due to resin polymerization, making it challenging to isolate those compounds from the paper. When the ink is applied on paper, it initiates a series of transformations, such as solvent evaporation, dye degradation, and resin polymerization, until equilibrium is established and no further changes occur. Comparing the ink inside the pen cartridge or on a recent application with the ink placed on paper for some time is what dynamic ink dating analysis does. Analyzing the transformations that occur makes it possible to determine the length of time the ink has been on the paper. Three instrumental ink dating and analysis methods exist: separation, mass spectrometry, and spectroscopy [13].

To meet the rigorous judicial requirements related to the age of documents, this article aims to examine the most prominent scientific publications about ballpoint ink characterization and dating over the past decade. This information could enhance the quality of forensic reports and facilitate further investigation.

This paper aims to perform a thorough and chronological review of ink age determination studies conducted between 2011 and 2020 to summarise the tools and techniques required to establish ink age. The paper is divided into two sections: determining the ages of ballpoint pen inks and non-ballpoint pen inks.

2. Findings

2.1 Determining the age of ballpoint pen inks

2.1.1 Work done between 2011 to 2015

GC was the primary technique for analyzing pen ink components, with high-performance liquid chromatography (HPLC) and UV-visible spectroscopy closely following. These methods were employed to study the composition of inks, including dyes and solvents. In a study by Weyermann and co-workers, innumerable ink dating methods suggested in prior research papers were examined [22]. In another study, using principal component analysis (PCA) to classify pens based on their infrared (IR) spectra has proven to be highly effective, particularly when differentiating between pens in short time frames [23]. Cantu [24], the equation developed for the drying process of inks, considers the ink comprising a non-volatile solute and a volatile solvent within a vertical container that is open on one side. According to this study, a specific point of maximum evaporation was identified. Before this point, evaporation occurred rapidly, whereas, after this point, the evaporation rate slowed down. This conclusion was drawn based on the study's assumptions or conditions.

These could relate to factors like solvent concentration, environmental conditions, or the interaction between the solvent and solute within the ink. However, specific effects that suppress the evaporation rate, such as the polymerization of resins and the substrate structure, were not considered. Bugler and co-authors. [18] Developed a technique that was employed by Koenig and other researchers [25]. The results for repeatability of the samples at three distinct ages showed considerable variation. The study employed exponential regression models to analyze the evaporation process of inks. Through these models, the half-life of evaporation was calculated using plotted data, which then facilitated the classification of inks into two categories based on their drying speed: fast-drying or slow-drying. The rate at which the ink aged was not affected by the amount of PE present. Despite a significant duration since the ink was applied to the paper, a small quantity of Phenoxyethanol persisted within the paper substrate. Another study compared four distinct parameters involved in the aging process of ink (ballpoint pen) under natural and artificial conditions-controlled aging. Before the analysis, the methods were validated for repeatability and reproducibility. Measuring the amount of PE using RPA methods yielded significant results [26].

Roman and co-author [27] created the dating ink method DATINK to determine the definite age of ink. Over five years, they validated the technique, achieving promising results. Continuing his prior work, Cantu [28] modified the ink-drying process model to include the evaporation dynamics of different scenarios: Ink on a glass slide, a saturated solution, an imperfect solution, and an absorbent substance. The necessary modification has been made to account for various conditions that affect ink evaporation. The transition from an ideal to a non-ideal solution caused a shift in the maximum acceleration point on the drying curve. On a flat, non-absorbent surface, gravity influenced the shape of a deposited solution drop, resulting in a hemispherical configuration. The surface area decreased as the exposed surface evaporated, causing the drop to flatten. The solvent diffused into the material on an absorbent surface, leaving the solute behind. This diffusion process led to diffuse solutes and increased evaporation due to the large surface area and the diffusion of solvents into the porous substrate. The proposed model bore a significant resemblance to the one developed by researchers [15] and delivered good correlations when tested against real-world samples [28]. However, findings obtained from the study of controlled environments might not precisely reflect what occurs in actual situations. Ink aging is influenced by evaporation, diffusion, adsorption, volatilization, and diffusion, among others [22]. Furthermore, ink composition, the amount of ink at the start, its surface, and its storage affect how ink ages. [22, 25, 26, 28]. Air flux, temperature, and Humidity also affect aging; thus, climatic chambers do not accurately represent natural conditions [25]. **Table 1** provides the instrument specifications, sample details, and components studied.

Table 1: Studies on ballpoint pen inks from 2011 to 2015

S. No.	Name of Instruments	Samples	Findings	Year
1.	ShimadzuUV-Vis Spectrometer Perkin-Elmer IR Spectrophotometer Thin Layer Chromatography High Performance Thin Layer Chromatography	Ballpoint pen ink dissolved in ethanol, and ballpoint pen ink strokes dissolved in ethanol.	Crystal Violet and Methyl Violet dyes	Senior and Co-researchers (2012)
2.	TDS3 Thermal Desorption unit attached to Agilent 6890N-MSD 5973N Gas Chromatograph Mass Spectroscope	5mm × 1mm ballpoint pen ink line on 80GSM white sheet	2-phenoxyethanol (PE)	Koenig and Co-researchers. (2014)
3.	Agilent 6890 Gas Chromatograph - 5790 C Mass Spectrometer	1cm Ballpoint pen ink line on 80 GSM white sheet extracted in 15 µl chloroform containing PE-D2	Solvents	Koenig and Co-researchers (2015)
4	Multiple Headspace Solid Phase Micro-extraction Agilent 6890 Gas Chromatograph 5973-N Mass Spectroscope	A variable number of 1.20 mm discs of Black and blue ballpoint entries on a white paper were extracted at 90 °C for 15 mins.	Volatile solvents	Roman and Co-researchers (2015)

2.1.2 Work done between 2016 to 2020

Gas chromatography, HPLC, UV-visible, and Raman spectroscopy commonly analyze pen ink's dye and solvent components. Researchers have been able to differentiate between artificially and naturally aged samples up to 6 months by detecting the degradation of various components into monomeric fragments [29]. These fragments are then used to identify the type of aging condition. A study found that HPLC-MS was more appropriate than SPME-GC-MS, even

though both techniques complemented each other. The intensity of the degradation trend varied under different aging conditions [30]. Raman spectroscopy is an effective method for ink samples over six months old. The inks were studied in natural and artificial aging conditions and categorized accordingly. By analyzing the degradation of ink samples over a long period, researchers found that the aging of ink is associated with the transformation of the dye matrix, demethylation, and photo-oxidation. Sharma and Kumar [31] conducted multiple linear regression (MLR) analysis, testing different parameters against different models to estimate the curve. Using PCA, they selected loading value and average temperature as the variables for the MLR model, which led to a significant reduction in the error rate. Some researchers analyzed 30 organic compounds and evaluated their concentrations over time to identify two aging phases for ink: the 1st for a maximum of 30 days and the 2nd for more than 30 days. Methyl violet b base, benzyl alcohol, and Phenoxyethanol were the most plentiful organic compounds [32]. In a study, pen inks were classified based on the type of dye. They performed chromatographic analysis after spectroscopic analysis and found that Raman spectroscopy could determine the ink age beyond 1.5 years without sample preparation. However, comparing samples aged naturally and those aged in high temperatures wasn't trustworthy." The absorption values in the multiple linear regression model decreased with time. Even though the numbers were different at different light wavelengths, we could only reliably use the multiple linear regression technique for blue ballpoint pens that were over a year old. [33]. Researchers calculated and compared seven parameters to date ink samples over one-year-old. Determining the age of the ink required using multiple methods and comparing the outcomes. Statistically significant organic compounds, such as phenoxyethanol, benzyl alcohol, and methyl violet base, were identified by applying variance analysis and multiple regression models to help analyze the ink age [34]. Three interpretation models were tested using different aging parameters: the threshold method, trends approach, and likelihood ratio calculation. The previous study had yielded encouraging findings with these parameters. The ink composition determined the initial concentration of Phenoxyethanol and R%, with higher concentrations of Phenoxyethanol indicating newer inks. However, lower concentrations of PE only sometimes meant older inks. Similarly, higher R% values suggested younger inks but not vice versa. Although both parameters correlated, R% values showed more variation than PE. RNORM values decreased over time, but they were distinct from R% values. Additionally, RNORM and Phenoxyethanol showed a correlation. NR% values were insignificant for the week-old sample, and no correlations were found with other parameters. The NRNORM values and RPA had different results, but they only worked for young ink samples. However, implementing the substitute R %* was involuted and yielded insignificant results compared to R% [35].

Establishing threshold values for ageing parameters was based on ageing situations to avoid errors. Threshold values needed optimization, which was done by conducting t-tests and analyzing the kinetics of ink aging. Multiple ink analyses were required for this purpose. However, t-tests performed on Phenoxyethanol, RNORM, and R% were unsuccessful due to high variability. Conducting these tests only after completing prior tests on extensive ink samples was recommended. The probability of the document's authenticity was determined by calculating the likelihood ratio. This led to the document being classified as old, incompatible, or young. It has been observed that Phenoxyethanol, in large amounts, is categorized as a fresh ink sample, while smaller amounts are deemed insufficient for older ink samples. The R% likelihood ratio has been found to be the least reliable and error-prone. The RNORM technique has been proven to be the finest method for determining ink age, providing error-free outcomes [35]. A study analyzed the kinetics of PE by exposing the samples to different temperatures using two distinct modes. The first method involved increasing the injector temperature from 100°C to 150°C, then to 200°C, and finally to 225°C at an interval of four minutes each. The second method involved increasing the injector temperature from 100°C to 200°C at an interval of six minutes [36]. Some authors determined phenoxyethanol in pen inks by naturally aging them for up to 3 years, exposing them to natural environmental conditions, or storing them in closed conditions. They artificially aged the samples at 24°C and 70°C for one hour [37]. To establish a relationship between artificial and natural aging, samples were exposed to a Xenon Lamp in Solar Box 1500e RH for up to 257 hours. Different statistical parameters were also tested to validate the PLS model. [38]. In a study, researchers used visible spectroscopy to analyze pen ink writings stored in three different environmental conditions for up to 32 months. The experiment involved exposing the conditions to light, darkness with exposure to air, and darkness without exposure to air. The concentration of phenoxyethanol was found to be dependent on the temperature rate of enlargement, and the primary peak was sharp. Over time, the desorption of phenoxyethanol decreased, but the relative quantity of phenoxyethanol increased at higher temperatures [39]. Fresh samples exhibited a rapid decrease in PE [36-37, 39]. It was found that the age of pen inks cannot be determined using Docucenter and spectroscopic methods [37]. During spectral analysis, distinctive UV-visible and near-infrared bands that reported the distinct rates and mechanisms of dilapidation of old and fresh ink samples were observed. The correlation between natural and artificial aging was calculated to be 143 hours and 1 hour, respectively [38]. However, the outcome of the analysis was influenced by various factors, such as humidity, temperature, storage conditions, and initial ink composition

[31, 39]. In 2017, a study presented a case that involved determining the age of a section of a document produced in 1996 by analyzing the ball pen ink used in the document [41]. To achieve this, the researchers generated plots and evaluated the dyes' retention time and peak areas. They discovered that the results for the part of the document differed from the rest, indicating that the two writings were created at other times. The V % values were evaluated, and a diagram was created that revealed the age of the questioned part to be approximately 6-8 months old. The significant time difference between the two writings was crucial in resolving the issue. Islek and co-researchers also presented another case where ink age analysis was used to investigate a bond written with a ball pen [40]. The payment date and the date of bond production did not match, which raised concerns that the dates were intentionally changed. Signature and handwriting samples were collected from the bond to determine the ink age. Peak areas were obtained, and plots were created for both samples. The data was used to calculate different ratios for both samples, indicating that the pen ink entries were made at various times. The instrument specifications, sampling information, and components studied are detailed in **Table 2**.

Table 2: Studies on ballpoint pen inks from 2016 to 2020

S. No.	Name of Instruments	Samples	Findings	Year
1	SPME- Shimadzu GC-2010 Shimadzu GCMS-QP 2010 detector	NA	Volatile solvents and dye components	Freidenfelds and Co-researchers (2016)
	Waters Alliance 2695 with Waters QuatroMicroTM API			
2	Senterra Raman spectrometer equipped with a laser module confocal microscope	1cm ballpoint pen ink stroke on paper extracted in the 2 ml DMFA for 2 hours at room temperature	Dye and pigment components	Gorshkova and Co-researchers (2016)
	Chromatec-Crystal 5000.2 chromatograph equipped with flame ionisation detector			
	Thin Layer Chromatograph (TLC)			
3	Shimadzu UV–2550 series Spectrophotometer	5cm blue ballpoint pen ink was extracted overnight using 10 ml ethanol.	Dyes and solvents	Sharma and Co-researchers (2017)
4	Agilent Technologies 6850N/5975C gas chromatograph equipped with deconvolution reporting A.0400 and NIST v.2.0. Mass Spectral Library-AMDIS	8 × 1.25 mm Ballpoint pen ink entry on 80 GSM white sheet extracted with 15 µl methanol solution containing 0.1mg/l internal standard (3-methyl phenol)	Solvent and Dye components	DíazSantana and Co-researchers (2017)
	Agilent series 1260 Infinity HPLC system equipped with DAD Detector			
5	SenterraRaman spectrometer equipped with a laser module confocal microscope Chromatec-Crystal 5000.2 chromatograph equipped with flame ionisation detector	3×10mm ballpoint pen ink stroke on paper extracted in the 2 ml Dimethyl Formamide (DMF) for 2 hours at room temperature	Dye and pigment components	Grechukha and Co-researchers (2017)
6	Waters™ 2690 separations Module	0.1 mg of fresh ink/ 7 punches of artificially aged ink extracted in 1ml MeOH	Dye components and volatile components	OrtizHerrero and Co-researchers (2018)
	Cary 5000 UV–visNIR spectrophotometer coupled with DRA-CA-5500 integrating sphere	A 1 cm diameter ink sample was placed on a spread 80 GSM white sheet using a brush.		
7	Agilent 6890 Gas Chromatograph - 5790 C Mass Spectrometer	1cm Ballpoint pen ink line on 80 GSM white sheet extracted in 15 µl chloroform containing PE-D2	Solvent and Dye components	Koenig and Co-researchers (2018)
8	Thermo Scientific DegazerSystem SCM 1000 with Pump Spectra System P1000	Ballpoint pen ink entries extracted in 100 µl of methanol	Dye components	Islek and Co-researchers (2018)
9	4000 UV-visible spectrophotometer with DRA-900 Internal Diffuse Reflectance	25 mm2 ballpoint pen ink entries on white sheets	Dye components	Sauzier and Co-researchers (2018)
10	Agilent 6890 gas chromatograph equipped with a 5973 series mass selective detector	0.3–0.4 mm ballpoint pen ink line on 80 GSM white sheets.	2-phenoxyethanol	Andrasko and Co-researchers (2018)
11	Agilent 6890 gas chromatograph equipped	1 cm ballpoint pen ink entry on	2-phenoxyethanol	EL-Sabbah and Co-

	with an Agilent mass spectrometric detector	80 GSM A4 white sheets extracted with 10ml carbon tetrachloride with acetonitrile (weak) and 10 ml chloroform with acetonitrile (strong)		researchers (2019)
12	Unity Thermal Desorber Agilent HP 6890N GC 5975B MS Thermo Scientific Degasser System SCM 1000, Pump Spectra System P1000	1.2 mm ink entry extracted in methanol	Crystal violet and phenoxyethanol	Islek and Co-researchers (2020)

2.2 Determining the age of Gel pens/ Fountain pens/ Iron gall pens/Rollerball pens

2.2.1 Work done between 2011 and 2015

Various methods were used to analyze pen ink's dye and solvent components, including laser desorption ionization, thin-layer chromatography, high-performance liquid chromatography, microscopy, and gas chromatography. Wu and co-workers [46] distinguished gel pen inks based on the presence of surfactants and classified ink samples by their mass number or mass-to-charge ratio. To identify dye components of different inks, precedent, and parent ions were studied positively. A recent study [47] has successfully distinguished between different types of gel pen inks by analyzing the number of peaks and their retention time. The researchers used the dissolution-diffusion method to determine the composition of black gel pen inks and examine their aging process. It was discovered that there are four types of gel pen inks, which were classified based on the number of spot rings, their color, and their radius on thin-layer chromatography plates [48]. Iron gall inks use the dissolution-diffusion method for up to twenty months. As time progressed, the relative intensities of dye components decreased while the relative intensities of degradation products increased [49]. Degradation occurred more slowly under natural aging than under artificial conditions [46-47]. Due to the varying boiling points of different solvents, a connection between natural and artificial aging can be observed. The dissolution-diffusion rate was higher for fresher ink and lower for older ink [48]. The speed at which the ink dissolves and spreads is influenced by several factors, such as the amount of ink components used, the type of surface it was applied on, the thickness of the ink stroke, and the way it was stored [48-49]. **Table 3** contains information on the instrument specifications, sampling details, and components studied.

Table 3: Studies on non-ballpoint pens from 2011 to 2015

S. No.	Name of Instruments	Samples	Findings	Year
1	High Performance Liquid Chromatography Quadruple-Time of Flight-Mass Spectrometer Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer	5cm gel pen ink line sample extracted Dimethyl formamide (DMF) for 12 h	Dye components	Wu and Co-researchers (2012)
2	Thin Layer Chromatography Motic-microscope equipped with Reflective Light Source.	1cm Black Gel pen ink lines on three kinds of paper were extracted with DMF, Dioxane, and Ether (3:7:14) for 1 min.	Dye components/ entire ink	Li and Co-researchers (2014)
3	Agilent gas chromatograph equipped with a flame ionisation detector	20 × 1mm black gel pen ink line extracted in 10 µl methanol containing ethyl benzoate.	Volatile solvents	Li and Co-researchers (2014)
4	Thin Layer Chromatography Motic microscope	1cm pen ink line extracted in a solution of butanone, ether, and 5% oxalic acid (10:8:19). Samples were directly analysed under a microscope using the dissolution diffusion agent (2ml DMF, 7ml surface active agent, 13ml anhydrous ethanol, and 13g TiO power)		Li and Co-researchers (2015)

2.2.2 Work done between 2016 and 2020

Gas chromatography (GC) was the primary method used to analyze the solvent components of pen inks, followed by Raman spectroscopy and liquid chromatography. The gel pen inks that contained polyethylene glycol (PEG) oligomers were identified and dated by analyzing the m/z of the oligomeric PEG. [50]. Researchers have investigated the effect of natural environmental conditions on the solvent content of Pilot® rollerball pen inks that contained 2-Pyrrolidone (2-PD) solvent [51]. Additionally, they have examined the aging process of trimethylene glycol in carbon-based gel pen inks. The pens were divided into three groups based on the amount of TEG present [52]. The aging of ink samples was attributed to the loss of TEG, and LC-HRMS was a more efficient classification method than Raman spectroscopy. Over time, PEG oligomers degraded, resulting in a mass-by-charge ratio shift. As time passed, the quantity of low molecular-weight oligomers increased. The degradation rate of artificially aged samples was faster than that of naturally aged samples [50]. All paper and ink types, apart from those containing non-volatile binders, suffered a 2-point density loss over time. However, inks with non-volatile binders kept the appropriate level of solvent compatibility even with years of aging. At the point of intersection, the ink layer thickness was twice as thick as a single stroke. It took roughly twice as long for the ink solvent in the thicker ink layer to break down as in the smaller ink layer. Samples analyzed from the proximity of the ink stroke showed similar results [51]. The solvent diffusion and storage condition had an impact on the process. Initially, the degradation rate was high, but it gradually slowed until the curve straightened out, as mentioned in references [51-52]. Some researchers used multispectral imaging to date ancient documents formed with iron gall ink from the seventeenth to the twentieth century. A multispectral imaging system digitized the original documents, and 8th images were captured for every single document at several wavelengths of light. UV and IR light features were more effective than visible light features. The analysis of the characteristics obtained from UV and IR light extraction followed. The Kernel discriminates learning algorithm was utilized to perform ordinal classification, where most documents were classified accurately. It was feasible to differentiate between different year levels [53]. The sampling details, instrument specifications, and components studied are listed in **Table 4**

Table 4: Studies on non-ballpoint pen inks from 2016 to 2020

S. No.	Name of Instruments	Samples	Findings	Year
1	Thermo Fisher Scientific UltiMate 3000 UHPLC and a Q Exactive ™ Orbitrap mass spectrometer Renishaw Raman spectrometer	10 × 0.5 mm black gel pen ink entry on 80 GSM white sheet extracted with 80 µl DMSO. PEG 400 diluted in methanol.	Polyethylene Glycol (PEG) oligomers	Sun and Co-researchers (2017)
2	Agilent 6850 gas chromatograph interfaced with an Agilent 5975C mass selective detector	3 × 0.5 mm discs of ink on various types of papers extracted in 2 µl chloroform containing (up to 0.2 ng/µl) deuterated phenoxyethanol (internal standard)	2-pyrrolidone	Aginsky (2017)
3	Agilent 7890A GC system equipped with a flame ionisation detector (FID) Thermo Fisher Scientific Trace 1300-ISQ Gas Chromatograph Mass Spectrometer	0.5 cm carbon-based black gel pen ink entry on 80 GSM A4 white sheets extracted with 10 µl of methanol or methanol containing 5 µg/ml of ethyl benzoate (internal standard)	Triethylene glycol (TEG)	Ni and Co-researchers (2020
4	MS imaging system	NA	NA	Rahiche and Co-researchers (2020)

3. DISCUSSION

Researchers have dedicated considerable effort to studying ballpoint pen inks and their aging characteristics in the last decade. They have shared their findings and discoveries in this area, contributing significantly to the field. One of the main challenges in studying ink aging is the inability to accurately replicate writing and storage conditions, which makes it challenging to estimate the relative age of ink samples. Another factor that complicates the matter is that the storage conditions of certain documents are not constant, which means that some assumptions about ink aging may be false. Ink

aging is a complicated process influenced by various factors, such as the type of ink composition, storage conditions, substrate, and thickness of ink entries affecting the aging process. Therefore, comparing naturally aged samples with artificially aged samples is challenging and requires careful analysis and interpretation. When exposed to light or heat, ink can change composition, leading to unexpected outcomes during natural aging. One study proposed a link between natural, UV-induced, and heat-induced aging, which could help differentiate artificially aged documents from naturally aged ones. However, the composition of pen inks differs across brands and models, and their aging characteristics tend to show similarities. Therefore, it's crucial to directly examine samples from the paper itself because solvent extraction might lead to undesirable effects or alterations in the analysis. Understanding the initial composition of the ink sample is crucial for exploring the reproducibility of the testing method.

Aging ink involves a complex process, so validating aging methods is vital. This includes assessing inter-laboratory analysis and error rates and establishing quantification limits. Creating a database for various ink samples is essential. A reliable conclusion can only be drawn after examining an adequate sample size over a sufficient time interval. Interpreting results should rely on sound reasoning supported by factual evidence and logical deductions. According to Koenig and co-workers, the top way to figure out ink age is by calculating RPA values and the solvent loss ratio. However, according to Koenig and Weyermann, methods measuring phenoxyethanol quantity, RNORM, and solvent loss ratio showed promising results. The best interpretation model was the likelihood ratio approach.

Despite the considerable effort researchers have put into studying ink aging, reliable techniques for determining the age of ink still need to be discovered. Most researchers have concentrated on analyzing the colorants or solvents within the ink, but their studies have been limited to ink samples under controlled lab conditions. There is a need for research that investigates the effects of normal storage conditions on ink aging, considering the random exposure of samples to both artificial light and daylight. When dating an ink sample, it's essential to consider factors like substrate type, ink entry thickness, ink composition, and storage conditions. Unfortunately, only a few methods have successfully determined ink aging over an extended period. Usually, these methods deliver the most accurate results for ink aging within about six months. However, some researchers have successfully determined ink aging for up to 5^{th} years using the DATUVINK method, DATINK method and variations of its relative intensities [28, 36, 48]. Researchers should combine different methods and employ statistics and chemometrics to develop a universal technique for all ink brands and types. Additionally, it is essential to study multiple components of ink to improve ink aging analysis. Overall, studying ink aging is a challenging but crucial task that requires collaborative efforts and constant improvement in techniques and methods.

4. CONCLUSION

Over the past decade, numerous studies have been carried out to determine the age of ink, but a perfect method has yet to be developed due to the complex degradation process of ink. Researchers have employed various analytical tools, such as gas chromatography, high-performance liquid chromatography, and spectrometric techniques, but they have yet to provide conclusive and objective results. Among these tools, gas chromatography is the primary tool for dating ballpoint pen inks. In contrast, high-performance liquid chromatography and various spectrometric techniques have been employed for non-ballpoint pen inks. However, most research has been focused on ballpoint pen inks, and only some studies have addressed stamp and non-ballpoint pen inks. Experts recommend researching printing inks and local writing instrument brands to understand ink aging better. Researchers suggest that more comprehensive research should be conducted on all ink types using faster and more affordable methods. Therefore, scientists worldwide must collaborate on this issue to draw better conclusions. It is hoped that such collaborations will lead to the development of a reliable and objective method for ink dating that can be used for various types of inks, enabling researchers to determine their age with greater accuracy.

REFERENCES

[1] Koenig, A., &Weyermann, C. (2018). Ink dating part II: Interpretation of results from a legal perspective. Science & Justice, 58(1), 31-46.

[2] Ezcurra, M., Góngora, J. M., Maguregui, I., & Alonso, R. (2010). Analytical methods for dating modern writing instrument inks on paper. Forensic Science International, 197(1-3), 1-20.

[3] LaPorte, G. M., & Stephens, J. C. (2011). Analysis techniques used for the forensic examination of writing and printing inks. Forensic chemistry handbook, 225-250.

[4] Neumann, C., Ramotowski, R., &Genessay, T. (2011). Forensic examination of ink by high-performance thin layer chromatography—The United States Secret Service Digital Ink Library. Journal of Chromatography A, 1218(19), 2793-2811.

[5] Calcerrada, M., & García-Ruiz, C. (2015). Analysis of questioned documents: a review. Analytica chimica acta, 853, 143-166.
[6] Kovalev, K. M. (2021). Determining the date of production of a document: historical aspect and modern trends. Forensic Bulletin , 35 (1), 19-37.
[7] Brunelle, R. L., & Crawford, K. R. (2003). Advances in the forensic analysis and dating of writing ink. Charles C Thomas Publisher.
[8] Aginsky, V. N. (1993). Some new ideas for dating ballpoint inks—a feasibility study. Journal of Forensic Sciences, 38(5), 1134-1150.
[9] Andrasko, J. (2001). HPLC analysis of ballpoint pen inks stored at different light conditions. Journal of Forensic Sciences, 46(1), 21-30.
[10] 10.Andrasko, J. (2002). Changes in composition of ballpoint pen inks on aging in darkness. Journal of forensic sciences, 47(2), 324-327.
[11] Díaz-Santana, O., Conde-Hardisson, F., & Vega-Moreno, D. (2018). Comparison of the main dating methods for six ball-point pen inks. Microchemical journal, 138, 550-561.
[12] Lociciro, S., Dujourdy, L., Mazzella, W., Margot, P., & Lock, E. (2004). Dynamic of the ageing of ballpoint pen inks: quantification of phenoxyethanol by GC-MS. Science & justice: Journal of the Forensic Science Society, 44(3), 165-171.
[13] Andrasko, J., & Kunicki, M. (2005). Inhomogeneity and aging of ballpoint pen inks inside of pen cartridges. *Journal of Forensic Sciences*, *50*(3), JFS2004436.
[14] Weyermann, C., Kirsch, D., Costa-Vera, C., & Spengler, B. (2006). Photofading of ballpoint dyes studied on paper by LDI and MALDI MS. *Journal of the american society for mass spectrometry*, *17*, 297-306.
[15] Weyermann, C., Kirsch, D., Vera, C. C., & Spengler, B. (2007). A GC/MS study of the drying of ballpoint pen ink on paper. *Forensic science international*, *168*(2-3), 119-127.
[16] Bügler, J. H., Buchner, H., &Dallmayer, A. (2008). Age determination of ballpoint pen ink by thermal desorption and gas chromatography–mass spectrometry. *Journal of Forensic Sciences*, *53*(4), 982-988.
[17] Weyermann, C., Almog, J., Bügler, J., & Cantu, A. A. (2011). Minimum requirements for application of ink dating methods based on solvent analysis in casework. *Forensic science international*, *210*(1-3), 52-62.
[18] Senior, S., Hamed, E., Masoud, M., & Shehata, E. (2012). Characterization and dating of blue ballpoint pen inks using principal component analysis of UV–Vis absorption spectra, IR spectroscopy, and HPTLC. *Journal of Forensic Sciences*, *57*(4), 1087-1093.
[19] Cantú, A. A. (2012). A study of the evaporation of a solvent from a solution—application to writing ink aging. *Forensic science international*, *219*(1-3), 119-128.
[20] Koenig, A., Bügler, J., Kirsch, D., Köhler, F., &Weyermann, C. (2015). Ink dating using thermal desorption and gas chromatography/mass spectrometry: Comparison of results obtained in two laboratories. *Journal of forensic sciences*, *60*, S152-S161.
[21] Koenig, A., Magnolon, S., &Weyermann, C. (2015). A comparative study of ballpoint ink ageing parameters using GC/MS. *Forensic science international*, *252*, 93-106.
[22] San Román, I., Bartolomé, L., Alonso, M. L., Alonso, R. M., &Ezcurra, M. (2015). DATINK pilot study: An effective methodology for ballpoint pen ink dating in questioned documents. *Analytica Chimica Acta*, *892*, 105-114.
[23] Cantú, A. A. (2015). Evaporation of a non-ideal solution and its application to writing ink aging. *Forensic science international*, *247*, 69-78.
[24] Freidenfelds, V., Certova, J., &Mekss, P. (2016). The Determination of Signs of Accelerated Ageing of Records made with Ballpoint Pen Inks by Using Chromatography Methods. *J. Forensic Res*, *7*(4), 337.
[25] Gorshkova, K. O., Tumkin, I. I., Myund, L. A., Tverjanovich, A. S., Mereshchenko, A. S., Panov, M. S., &Kochemirovsky, V. A. (2016). The investigation of dye aging dynamics in writing inks using Raman spectroscopy. *Dyes and Pigments*, *131*, 239-245.
[26] Sharma, V., & Kumar, R. (2017). Dating of ballpoint pen writing inks via spectroscopic and multiple linear regression analysis: A novel approach. *Microchemical Journal*, *134*, 104-113.
[27] Díaz-Santana, O., Vega-Moreno, D., & Conde-Hardisson, F. (2017). Gas chromatography-mass spectrometry and high-performance liquid chromatography-diode array detection for dating of paper ink. *Journal of Chromatography A*, *1515*, 187-195.
[28] Grechukha, N. M., Gorshkova, K. O., Panov, M. S., Tumkin, I. I., Kirillova, E. O., Lukianov, V. V., ... &Kochemirovsky, V. A. (2017). Analysis of the aging processes of writing ink: Raman spectroscopy versus gas chromatography aspects. *Applied Sciences*, *7*(10), 991.
[29] Koenig, A., &Weyermann, C. (2018). Ink dating, part I: Statistical distribution of selected ageing parameters in a ballpoint inks reference population. *Science & Justice*, *58*(1), 17-30.
[30] Koenig, A., &Weyermann, C. (2018). Ink dating part II: Interpretation of results in a legal perspective. *Science & Justice*, *58*(1), 31-46.
[31] Andrasko, J., & Lagesson-Andrasko, L. (2019). Simplification of Ink Dating for Forensic Analysis by Thermal Microdesorption Gas Chromatography–Mass Spectrometry. *Analytical Letters*, *52*(6), 972-982.

[32] El-sabbah, M. M., Gomaa, A. Z., & Al-Hawary, A. S. (2019). Dating the ballpoint pen inks using gas chromatography-mass spectrometry technique. *Egyptian Journal of Chemistry*, *62*(3), 385-400.
[33] Ortiz-Herrero, L., Bartolomé, L., Durán, I., Velasco, I., Alonso, M. L., Maguregui, M. I., &Ezcurra, M. (2018). DATUVINK pilot study: A potential non-invasive methodology for dating ballpoint pen inks using multivariate chemometrics based on their UV–vis-NIR reflectance spectra. *Microchemical Journal*, *140*, 158-166.
[34] Sauzier, G., McGann, J., Lewis, S. W., & Van Bronswijk, W. (2018). A study into the ageing and dating of blue ball tip inks on paper using in situ visible spectroscopy with chemometrics. *Analytical Methods*, *10*(47), 5613-5621.
[35] İslekSalkım, D., İşat, E., & Cengiz, S. (2018). Ink ag. *Research Journal of Forensic Sciences*, *6*(5), 1-4.
[36] SalkımİşIek, D., İşat, E., & Cengiz, S. (2020). Determination of changes in crystal violet and phenoxyethanol (dating ink). *Journal of Forensic Sciences*, *65*(2), 661-663.
[37] Wu, Y., Zhou, C. X., Yu, J., Liu, H. L., & Xie, M. X. (2012). Differentiation and dating of gel pen ink entries on paper by laser desorption ionization-and quadruple-time of flight mass spectrometry. *Dyes and Pigments*, *94*(3), 525-532.
[38] Li, B., Xie, P., Guo, Y. M., & Fei, Q. (2014). GC analysis of black gel pen ink stored under different conditions. *Journal of Forensic Sciences*, *59*(2), 543-549.
[39] Li, B. (2014). Dating of black gel pen ink using the dissolution–diffusion method. *Forensic Science International*, *234*, 126-131.
[40] Li, B., & Xie, P. (2015). Dating of Iron Gall Ink Using the Dissolution-Diffusion Method. *Journal of forensic sciences*, *60*(2), 476-481.
[41] Sun, Q., Luo, Y., Xiang, P., Yang, X., & Shen, M. (2017). Analysis of PEG oligomers in black gel inks: Discrimination and ink dating. *Forensic science international*, *277*, 1-9.
[42] Aginsky, V. N. (2017). Dating Water-Based Inks on Documents—Rollerball Pen Inks Containing Pyrrolidone. *J Am Soc Questioned Doc Exam*, *20*(2), 11-30.
[43] Ni, Y., He, N., Lü, Y., Zou, N., Song, H., Li, H., & Zhao, P. (2020). Study of ink aging: Targeting triethylene glycol in carbon-based black gel ink strokes on paper. *Forensic science international*, *311*, 110296.
[44] Rahiche, A., Hedjam, R., Al-Maadeed, S., & Cheriet, M. (2020). Historical documents dating using multispectral imaging and ordinal classification. *Journal of Cultural Heritage*, *45*, 71-80.