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Studying the Methods to Determine the Age of Ink: A Critical Review of Ink Dating Methods

دراسة طرق تحديد عُمر الحبر: مراجعة نقدية لطرق تأريخ زمن الحبر

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Abstract

On the basis of the type of ink, pen inks are classified as ballpoint pens or non-ballpoint pens. Ballpoint pen inks are oil-based inks (ballpoint pens). While non-ballpoint pen inks are water-based inks (gel pens, fountain pens, pilot pens, fiber tip pens, etc.). Different approaches related to the determination of the age of ink were proposed in the literature, including ballpoint pen inks, non-ballpoint pen inks and stamp pad inks. This study provides a comprehensive appreciation of analytical research studies that were published from the year 2000 to year 2020 on the determination of the age of inks. Owing To contemporary technological advancements, the process has been developed in many folds. However, its reliability is questioned due to the variability in methods and results. Research works related to the aging of ink have been compiled to assist the researchers and the forensic document examiners and to provide an overall insight regarding the works done so far. In an attempt to unravel this issue of questioned document examination, a critical and systematic review of the literature is proposed to encourage the usage of various tools and techniques necessary to establish the age of ink in different case works.

Keywords: Forensic science, questioned documents, determination of the age of ink, pen ink, stamp pad ink.

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المستخلص

يتم تصنيف أحبار الأقلام وفق نوع الحبر المستخدم فيها إلى قسمين: أقلام برأس كروي وأقلام بدون رأس كروي. حيث تكون أحبار الأقلام ذات الرأس الكروي أحباراً زيتية، بينما تكون أحبار الأقلام دون رأس كروي عبارة عن أحبار مائية، مثل: أقلام الحبر الهلامي (جل)، وأقلام الحبر السائل (أقلام الريشة)، وأقلام ماركة بايلوت، وأقلام بطرف لباد، إلخ. تم اقتراح طرق مختلفة تتعلق بتحديد عمر الحبر في الدراسات السابقة، بما في ذلك أحبار قلم الحبر بالرأس الكروي، وأحبار أقلام الحبر بدون رأس كروي، وأحبار الأختام. و تقدم هذه الدراسة تقديراً شاملاً للدراسات البحثية التحليلية التي تم نشرها من عام 2000 إلى عام 2020م حول تحديد عمر الأحبار. بسبب التطورات التكنولوجية المعاصرة، وقد تم تطوير هذه العملية بشكل مضاعف. ومع ذلك، فإن موثوقيتها موضع تساؤل بسبب التباين في الأساليب والنتائج. كما تم تجميع الأعمال البحثية المتعلقة بتقدير عمر الحبر لمساعدة الباحثين وفاحصي الوثائق الجنائية ولتقديم نظرة شاملة حول الأعمال التي تم إنجازها حتى الآن. من أجل محاولة حل المشاكل التي تتعلق بفحص المستندات المشكوك فيها، وتم اقتراح إجراء مراجعة نقدية ومنهجية للدراسات السابقة لتشجيع استخدام الأدوات والتقنيات المختلفة اللازمة لتحديد عمر الحبر في أعمال الحالات المختلفة.

الكلمات المفتاحية: علوم الأدلة الجنائية، المستندات المشكوك فيها، تحديد عمر الحبر، حبر القلم، حبر وسادة الختم.

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1. Introduction

Forensic document examiners are often presented with challenging issues which become mandatory to be resolved for the progress of investigations and judicial information, and therefore require a thorough knowledge of the subject and expertise in the field. Document cases related to determination of age of ink are among those issues. Determination of age of writing ink (in question) refers to the assessment of probable time when ink had been placed on the paper. This may become tedious due to a great variety of writing inks available in the market. The examination becomes more complicated due to the complexity of chemical processes that take place with time after the deposition of ink and the effect of external factors like storage conditions, light, temperature, humidity, etc. [1].

Various types of writing instruments can be used to produce documents of legal importance like wills, contracts, agreements, testaments, etc. Inks of these pens are either oil-based, or water-based [2]. Pagano et al. [3] classified writing inks into two categories namely ballpoint pen inks and non-ballpoint pen inks. Inks are composed of colorants, vehicles, resins, and additives. A colorant is mainly dye or pigment, which is used to provide colour to the ink. A vehicle acts as a carrier. Chief carrier in non-ballpoint pen inks is water, while ballpoint pen inks use oil as carrier. Certain other solvents may also be used along these carriers. Resins contribute to the viscosity, adhesion, rheological properties, etc. [4].

One important feature of an ink is its static profile. Static profile of an ink refers to the properties which do not change with time. It can be generated by the determination of optical properties, specific tags used in inks, and anachronism. However, dynamic profiling is performed to assess the probable age of an ink sample. It involves evaluation of changes that occur in different components of an ink [2]. As the ink gets deposited onto the paper, various physical and chemical changes occur, such as degradation of colorant, evaporation of solvent, and hardening or polymerisation of resins and additives. Techniques used in forensic science require that the results should be accurate and repeatable [5].

The researchers have also introduced the concept of static approach, relative approach, and absolute age approach to determine the age of ink. Static approach deals with the stable components of the ink [6]. Relative age is estimated on the basis of comparison, which requires the same ink, paper, and environmental conditions [6-7]. Absolute age is estimated on the basis of identification rather than comparison [8]. Various manufacturers of ink also introduce tags to the ink [5]. However, these are not found in all types of inks due to high cost. Also, a database for such tags would be required which is not available at present.

Iron gallotannate inks were prevalent from 1920 till 1972 and certain studies related to their dating were conducted. Prior to the year 2000, studies related to the determination of age of ballpoint pens were common. Cantu and Brunelle (1980); Cantu and Prough (1987); Brunelle et al. (1987), Brunelle and Lee (1989); Isaacs et al. (1990); Aginsky (1993); Aginsky (1994); Brunelle (1995) studied resins present in the ballpoint pens. Stewart (1982); Humecki (1985); Cantu (1988); Aginsky (1993); Aginsky (1994); and Aginsky (1997) worked on volatile components of ballpoint pen inks. Aginsky (1993, 1995) worked on dye components of ballpoint pen inks [5].

The study aims to carry out a comprehensive and a chronological review of research works related to the determination of the age of inks carried out from the year 2000 to the year 2020, to summarise the tools and techniques necessary to establish the age of ink. This paper has been divided into three sections including the determination of age of ballpoint pen inks, the determination of age of non-ballpoint pen inks, and the determination of age of stamp pad/ seal inks.

2. Review

2.1 Determination of age of ballpoint pen inks

2.1.1 Studies from the year 2000 to 2005

High performance liquid chromatography (HPLC) was the most used technique in this time frame followed by gas chromatography (GC), laser desorption ionisation (LDI), and matrix assisted laser desorption ionisation mass spectrometry (MALDI-MS) to study the dye and volatile components of ink. Crystal violet and methyl violet were the most common dyes present in all blue coloured ballpoint pen inks in various concentrations. On exposure to light, their concentration decreased and resulted in the formation of new products which were detected at 540 nanometers (nm). Demethylation of crystal violet led to the formation of methyl violet and further demethylation led to the formation of tetramethyl pararosaniline. Similar quantitative changes were noted when the samples were stored in dark conditions [9-10]. Ternary diagrams were prepared to study the relative changes in composition of the three dyes.

According to Fig. 1 Hofer. [11], hexamethyl-pararosaniline present in crystal violet dye decomposed to pentamethyl-pararosaniline, which further decomposed to tetramethyl-pararosaniline and lastly to trimethyl-pararosaniline. The concentration of ink components was dependent on the initial concentrations, which decreased with time [11]. The curves obtained for samples stored in dark were similar to samples stored in natural light. However, the changes observed in one day of natural light were analogous to changes observed over one month in darkness [10]. Lociciro et al. [12] explained that the ink dried in two phases. In the first phase, the ink had more solvent which diffused and evaporated. Heat and air affected the mechanism. In the second phase, the volatile solvents had already dried, and resin started to harden.

Andrasko and Kunicki [13] studied the aging of ballpoint pen ink inside the pen cartridge. Repeated analysis of ink by the same ballpoint pen was done over a period of six years. Relative age of ink in cartridge and composition of ink showed no correspondence, and relative concentration of dyes was unaffected in this time frame. It was suggested not to use initial strokes for examination [13]. MALDI-MS spectra were generated for pure methyl violet and ethyl violet dye samples by Weyermann et al. [14]. Under the influence of light, both dyes showed various degradation products. Relative peak areas were quantified. The composition of different pens varied and hence, their aging also showed different behaviour. Samples on paper showed better repro-

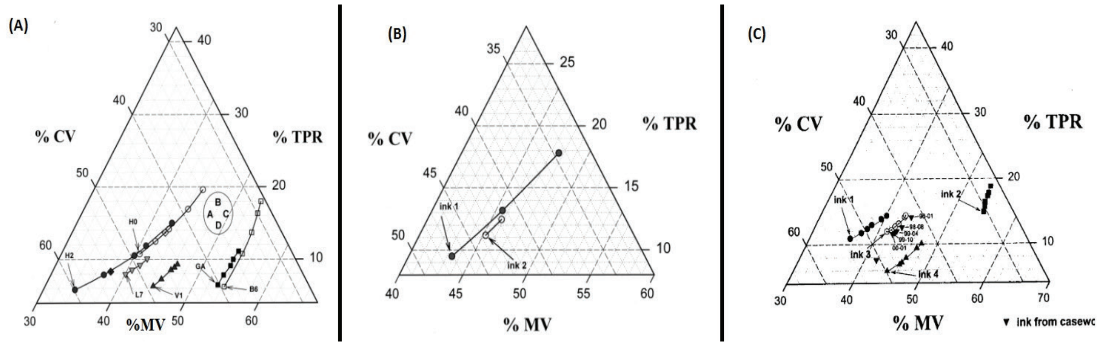

Figure 1 -*Ternary diagrams [9, 10].*

ducibility in LDI than the pure samples. Fragmentation was stronger for ethyl violet dye. Fig. 2 However, minimal changes were witnessed in samples stored in the dark, which was in correspondence to the results obtained by Andrasko [10].

Aging of dyes was dependent on heat, humidity, wavelength of light, ink, paper, ink thickness, paper matrix and seasons [10, 12, 14]. If the document to be dated had been exposed to a diverse amount of light, changes in composition due to aging surpassed the effect of light and it would be difficult to distinguish between aging due to light and aging due to darkness. This issue may also arise due to exposure to heat [10]. The specifications of instrument, sampling details and component studied are mentioned in Table 1.

2.1.2 Studies from the year 2006 to 2010

Gas chromatography (GC) was the most used technique followed by HPLC, liquid chromatography (LC) and matrix assisted laser desorption ionization (MALDI) to analyse dye and solvent components of pen ink. Weyermann et al. [15] identified various solvents in the initial ink composition of various pens. Fig. 2 Variation in the initial composition of different pens was noted using relative peak areas (RPA) and graphs. Samanidou et al. [16] identified and differentiated dye components on the basis of retention time and ultraviolet (UV) spectra in 360-596 nm range. Weyermann and Spengler [17] examined the prospects of artificial aging to replicate natural aging. For natural aging, samples were exposed to natural light at room temperature or in darkness. For artificial aging, samples were stored in an oven or exposed to xenon lamps. Bugler et al. [18] categorised inks as slow and fast aging inks on the basis of decrease in the solvent concentration ratio at different desorption temperatures.

Berger-Karin et al. [19] also compared aging of ballpoint pen inks in artificial and natural conditions. Weyermann et al. [1] proposed a statistical method to evaluate aging of ink by studying the quantity of

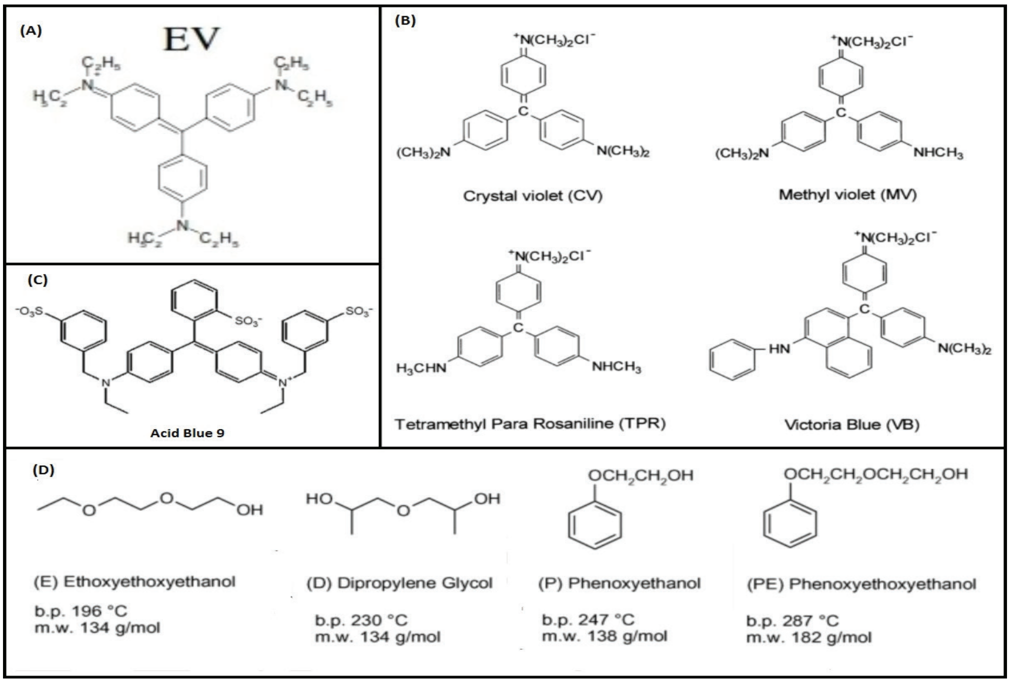

Figure 2- *Chemical Structures of (A) Ethyl violet [14]. (B) Blue dyes [9]. (C) Acid Blue 9 [5]. (D) Different solvents [15]*

Table 1- *Ink dating studies on ballpoint pen from the year 2000 to 2005.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Andrasko (2000)	Hewlett Packard series II Liquid Chromatography connected to the HP's HPLC 3D ChemStation	HPLC Column (Size of column)	TSKgel ODS-120T stainless steel column (25 cm × 4.60mm, 5µm)	Single asterisk/ letter containing about 1 cm ballpoint pen ink line on 80GSM white sheet extracted in 0.2 ml methanol	Dye components
		Detector	Hewlett Packard diode array detector		
		Mobile phase	Solution A: 20% acetonitrile and 80% water containing 10 mM KClO$_4$ (pH 3) Solution B: 100% acetonitrile		
	Varian Model 5000 Liquid Chromatograph	HPLC Column (Size of column)	Nucleosil C$_{18}$ (20 cm × 4.60mm, 5µm)		
		Detector	Variable wavelength detector (model 100)		
		Mobile phase	Solution A: 20% acetonitrile and 80% water containing 10 mM KClO4 (pH 3) Solution B: 100% acetonitrile		
Andrasko (2001)	Hewlett Packard series II Liquid Chromatography connected to the HP's HPLC 3D ChemStation	HPLC Column (Size of column)	TSKgel ODS-120T stainless steel column (25 cm × 4.60mm, 5µm)	Single asterisk containing about 1 cm ballpoint pen ink line on 80GSM white sheet extracted in 0.2 ml methanol	Dye components
		Detector	Hewlett Packard diode array detector		
		Mobile phase	Solution A: 20% acetonitrile and 80% water containing 10 mM KClO$_4$ (pH 3) Solution B: 100% acetonitrile		
Hofer (2004)	HP 1090	HPLC Column (Size of column)	RP-18 CC 150/4.6 Nucleosil 100–5 column	5mm ballpoint pen ink line extracted in 40 µL of methanol.	Dye components
		Software	AgiletChemStation software		
		Mobile phase	Potassium perchloride buffer (pH 3.0): methanol		
Lociciro et al. (2004)	Hewlett Packard G1800A GCD Gas Chromatograph Mass Spectroscope.	GC Column (Size of column)	DB-1 (30m × 0.25mm, 0.25µm)	10cm ballpoint pen ink line on 80GSM white sheet extracted in chloroform : pyridine : MSTF (5:1:1)	Volatile components
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	45°C - 280°C		
Andrasko et al. (2005)	Hewlett-Packard HP 1090 series II Liquid Chromatography connected to the HP's HPLC ^{3D}Chem-Station	HPLC Column (Size of column)	Zorbax SB-C18 stainless steel column (25 cm × 4.60mm, 5µm)	Single asterisk containing about 1 cm ballpoint pen ink line on 80GSM white sheet extracted in 30 µl methanol	Dye components and phenoxyethanol
		Detector	Perkin Elmer fluorescence detector (LC 240) in series with Hewlett Packard diode array detector		
		Mobile phase	Solution A: 20% acetonitrile and 80% water containing 10 mM KClO$_4$ (pH 3) Solution B: 100% acetonitrile		
Weyermann et al. (2005)	Home-built MALDI/ LDI reflector time-of-flight (TOF) mass spectrometer	Laser	337 nm pulsed nitrogen laser	5 × 8 mm paper with 2 to 3 strokes of ballpoint pen	Methyl violet and ethyl violet dyes
		Ion Mode	Positive		
		Mass resolving power	3000-6000		
	V-550 Jasco UV/ VIS spectrophotometer	Wavelength	190-900nm		
		Scan Rate	200 nm/ min		
		Resolution bandwidth	2nm		
		Cell	Quartz Suprasil (Hellma) precision cells		

solvents. Fig. 3 The concentration of phenoxyethanol (PE) decreased rapidly in the first few hours and then the concentration decreased gradually over time. The method was successful up to 4 months and made it easy to understand the complex pathway of ink aging. It was suggested to mention repeatability and error rates of the test and blind tests should be performed. Degradation was a result of demethylation and six degradation products of crystal violet with different molecular ions were detected [20]. Lalli et al. [21] detected five different dyes in blue ballpoint pen inks, of which basic violet 3 was common for all pens.

Solvents with higher boiling point tend to evaporate faster. Friction generated heat which led to the initial evaporation of the solvents. Diffusion of solvents depended on the viscosity of that solvent [15]. The samples stored in the dark did not show degradation for up to three years. Solvent loss was faster at higher temperatures and varied with ink composition. Hence, no model could be generated for correlation between natural aging and artificial aging due to the complex nature of the aging process [17]. In artificial conditions, at least 95% of PE evaporated under a desorption temperature of 200°C for 5 minutes. However, in natural conditions, a similar amount of PE evaporated in a few days and the rest evaporated slowly. Considerable inconsistency was observed in the solvent contents with respect to the amount and formulation of ink [18]. The observations made by Weyermann and Spengler [17] were not complementary to the observations made by Berger-Karin et al. [19]. The loss of PE was rapid in fast aging inks. However, it was sluggish in slow aging inks. The result of inks aging artificially corresponded to the result of inks aging naturally [19].

Phenoxyethanol solvent and crystal violet dye were most commonly used in ballpoint pens [1, 16, 18]. Few dye components showed the replacement of methyl and ethyl groups with hydrogen as they degraded with time, while few dyes remained unaltered and were used as a chemical clock. The degradation products of both the old and new ink were detected with the passage of time [21]. A wide range of samples must be analysed over a large time frame [16, 19]. Parameters like storage condition, composition, type of resin, and substrate affect the process of aging [15, 17-18, 20]. Hence, determination of precise age was difficult, but age boundaries could be established [15]. The specifications of instrument, sampling details and component studied are mentioned in Table 2.

2.1.3 Studies from the year 2011 to 2015

Gas chromatography (GC) was the most used technique followed by HPLC, and UV-visible spectroscopy to analyse dye and solvent components of pen ink. Weyermann et al. [22] scrutinized various ink dating methods proposed in previous studies Fig. 4 Senior et al. [23] classified pens on the basis of infrared (IR) spectra and principal component analysis (PCA). The technique was favourable for short time intervals. Fig. 4 An equation for the drying process of inks was developed by Cantu [24]. Ink was considered as a solution of a volatile solvent and a non-volatile solute, present in a vertical container open on one end. On application of ink, the solvent evaporated, making the solution more concentrated. Based on three assumptions, it was mathematically proven that there exists a point of maximum evaporation, before which the evaporation was fast and after which the evaporation was slow. Certain effects which suppress the rate of evaporation were not considered in the study, such as polymerisation of resins, and structure of substrate [24].

Koenig et al. [25] applied the method created by Bugler et al. [18]. High variability was observed when the samples were tested for repeatability at

Table 2- *Ink dating studies on ballpoint pen from the year 2006 to 2010.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Weyermann et al. (2007)	MAT 4500 Gas Chromatograph Mass Spectrometer	GC Column (Size of column)	CP-Sil 8 CB low bleed/MS capillary column (60m × 0.25mm, 0.25µm)	0.5mm × 1cm ballpoint pen ink line extracted using 10 µl dichloromethane	Volatile solvents
		Carrier gas (flow rate)	Helium (~3ml/min)		
		Min. – Max. Oven temp.	50°C - 300°C		
Samanidouet al. (2007)	LC-9A pump	HPLC Column (Size of column)	Inertsil ODS-3 (5m × 250mm, 4mm)	2cm ink line on A4 photocopy paper extracted using 0.5 ml acetonitrile	Dye components
		Detector	SPD- M6A photodiode array detector		
		Mobile phase	CH_3COONH_4, CH_3CN, CH_3OH (50:30:20 for 10 min and then 20:30:50 for 10 min and then 0:50:50 for 5 min)		
Weyermann et al. (2008)	MAT 4500 Gas Chromatograph Mass Spectrometer	GC Column (Size of column)	CP-Sil 8 CB low bleed/MS capillary column (60m × 0.25mm, 0.25µm)	1cm ballpoint pen ink line extracted using 10 µl dichloromethane	Dye components and Volatile solvents
		Carrier gas (flow rate)	Helium (~3ml/min)		
		Min. – Max. Oven temp.	50°C - 300°C		
Bugler et al. (2008)	TDS2 Thermal Desorption unit attached to Agilent 6840N-5973N Gas Chromatograph Mass Spectroscope.	Thermal desorption temperature	90°C - 200°C	5mm × 1mm ballpoint pen ink line on 80GSM white sheet	2-phenoxyethanol
		GC Column (Size of column)	HP5MS (30m × 0.25mm, 0.25µm)		
		Carrier gas (flow rate)	Helium (1.2ml/min)		
		Min. – Max. Oven temp.	45°C - 270°C		
Berger-Karin et al. (2008)	Atas Desorption System Optic III attached to Thermo-electron GC/ MS-system and Markes Desorption System attached to Agilent 6890N GC/ MS	Thermal desorption temperature	100°C (15 min), 140°C (15 min), and 200°C (10 min)	0.7–1.0 cm ballpoint pen ink stroke on paper	2-phenoxyethanol
		GC Column (Size of column)	ZB5ms Guardian		
		Carrier gas (flow rate)	Helium (1.2ml/min)		
		Min. – Max. Oven temp.	100°C - 320°C		
Weyermann et al. (2009)	Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometer	Laser	337 nm pulsed nitrogen laser	0.01 mg / mL pure BB3 dissolved in water or ethanol and 5-8 mm paper containing 2–3 ink strokes	Crystal violet dye
		Ion Source	Dual-stage ion mirror		
	V-550 Jasco UV/ VIS spectrophotometer	Wavelength	190-900nm		
		Scan Rate	200 nm/ min		
		Resolution bandwidth	2nm		
		Cell	Quartz Suprasil®Hellma® precision cells		
		Path Length	10 mm		
Lalli et al. (2010)	LCMS-2010EV Single Quadruple Mass Spectrometer equipped with home made Easy Ambient Sonic-Spray Ionization	Spray gas	Methanol and compressed Nitrogen (100psi)	Ballpoint pen inks on paper without any sample preparation or extraction	Dye components
		Flow rate	20 µl/min		

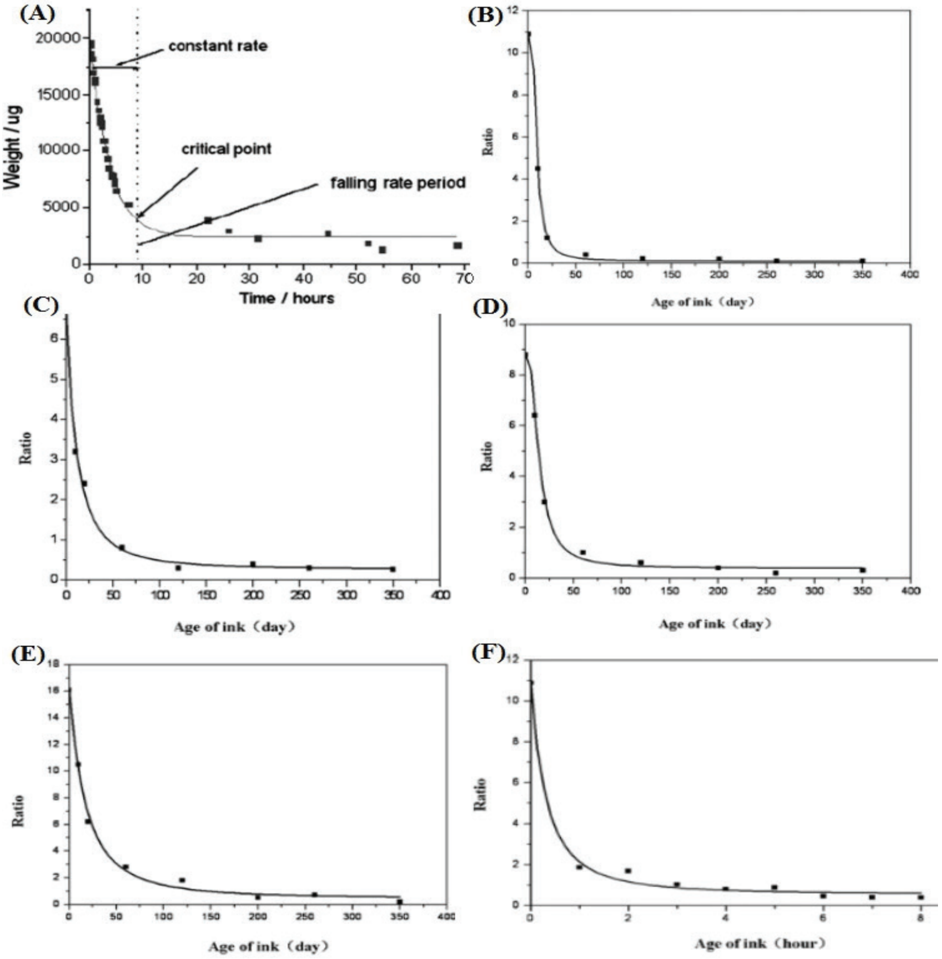

Figure 3- *Relationship between different solvent components and writing age of (A) ethoxyethoxyethanol [1]. (B) 1,2-Propylene glycol [48]. (C) Ethylene glycol [48]. (D) Diethylene glycol [48]. (E) Glycerol [48]. The slope is large during the first drying phase (constant rate) and continually diminishes after that (falling rate period).*

three different ages. Half-life was calculated using the plots and inks were classified as fast drying or slow drying inks. The samples followed an exponential regression. Aging speed was independent of the quantity of PE. Even after a long time of deposition of ink on paper, a small amount of PE stayed in the paper [25]. In another study, Koenig et al. [26] compared four different parameters of aging of ballpoint pen ink under natural and artificial aging conditions. Methods were validated for repeatability and reproducibility prior to the analysis. Significant results were obtained in case of measuring the quantity of PE and RPA methods [26].

Roman et al. [27] developed the ink dating methodology (DATINK) to estimate the absolute age of ink. Validation was carried out and promising results were obtained over a period of five years. Fig. 5 Cantu [28] in continuation to his previous work modified the model for drying process of inks by considering evaporation of a non-ideal solution, a saturated solution, a solution on a glass slide, and a solution on a porous substrate. When an ideal solution was changed to a non-ideal solution, the point of maximum acceleration on the drying curve was changed. When the drop of solution was placed on a flat nonporous surface, the solution formed

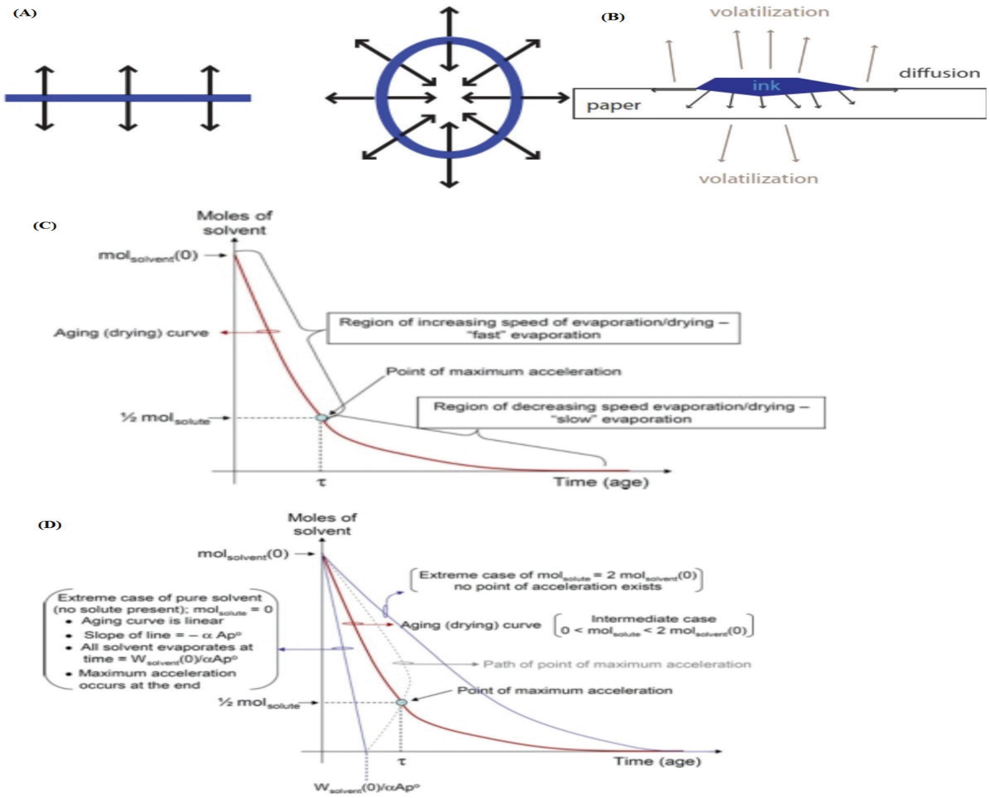

Figure 4- *Schematic representation of (A) solvent diffusion in case of a straight line and an oval stroke [22]. (B) Drying of ink [22]. (C) The aging curve of an evaporating solution in a pure solvent [23]. (D) A fast drying region and slow drying region of an evaporating solution [23].*

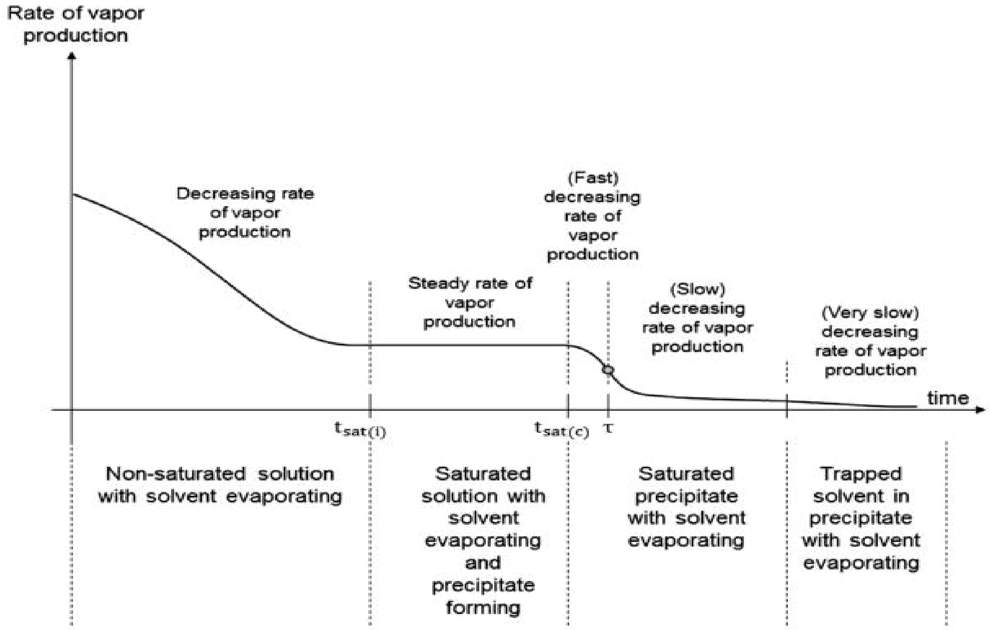

Figure 5- *Schematic representation of the rate of vapour production curve illustrating the four stages of the drying process [27].*

a hemispherical shape due to gravity. Evaporation took place from the exposed surface and the surface area decreased leading to the flattening of the drop of solution. When the drop of solution was placed on a porous surface, the solvent diffused into the surface leaving the solvent. Diffusion led to the spreading of solvent and increased rate of vapour production. This model was compared with the model proposed by Weyermann et al. [15] which was significantly similar. Good correlations were observed in real samples [28].

The results obtained for samples examined in a controlled environment must not be confounded to the real-life case samples. The examiner should validate the ink dating methods for repeatability, reliability, and logical interpretation [22, 25]. Drying of ink depends on factors like, evaporation, diffusion, adsorption, volatilization, and diffusion and these factors influence the aging of ink [22]. In addition to these, ink composition, initial ink quantity, type of substrate and storage conditions also affect the aging of ink [22, 25-26, 28]. Humidity, temperature, and air flux affected the aging and hence climatic chambers were not the true representative of natural conditions [25]. The specifications of instrument, sampling details and component studied are mentioned in Table 3.

2.1.4 Studies from the year 2016 to 2020

Gas chromatography was the most used technique in this time frame followed by HPLC, UV-visible spectroscopy and Raman spectroscopy to analyse dye and solvent components of pen ink. Freidenfelds et al. [29] differentiated naturally and artificially aged samples up to six months. Many components degraded into monomeric fragments, which were used to identify the type of aging condition. The results of high-performance liquid chromatography mass spectroscopy (HPLC-MS) were compared with those obtained by solid phase microextraction gas chromatography mass spectrometry (SPME-GC-MS). The trend of degradation was similar, but their intensity varied under different aging conditions. Both techniques proved complementary to each other. However, HPLC-MS was more suitable. According to Gorshkova et al. [30] Raman spectroscopy was an efficient technique for samples older than six months. Naturally and artificially aged ink samples were studied, and the inks were categorised. Spectra were obtained for a long time of degradation.

Transformation of dye Fig. 6 matrix, demethylation and photo-oxidation corresponded to the process of aging of ink [30]. Multiple linear regression (MLR) analysis was performed by Sharma and Kumar [31]. Fig. 6 Different parameters were tested against different models for the curve estimation model. On the basis of PCA, loading value and average temperature were selected as the variables for the MLR model. Multiple parameters were analysed and thus, the error rate was notably less. Díaz-Santana et al. [32] analysed 30 organic compounds and their concentrations were evaluated with respect to time. Two phases of ink aging were evident, first up to 30 days and second beyond 30 days. Phenoxyethanol (PE), benzyl alcohol (BZA) and methyl violet b base (MVBB) were the most abundant of all the organic compounds.

On the basis of type of dye, Grechukha et al. [33] classified the pen inks. Chromatographic analysis was done following spectroscopic analysis. Fig. 6 Raman spectroscopy helped to determine the age beyond 1.5 years and did not require sample preparation. The comparison of samples aged in natural conditions and those aged under high temperature was not reliable [33]. In the MLR model, the absorption values decreased with time. Although, the values were not consistent with varying wavelength [31]. MLR tech-

Table 3- *Ink dating studies on ballpoint pen from the year 2011 to 2015.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Senior et al. (2012)	Shimadzu UV-Vis Spectrometer	Wavelength	200-700nm	Ballpoint pen ink dissolved in ethanol and ballpoint pen ink strokes dissolved in ethanol	Crystal Violet and Methyl Violet dyes
		Scan Interval	1 nm		
		Cuvette (Path Length)	Quartz cuvettes (1 cm)		
	Perkin-Elmer IR Spectrophotometer	Frequency range	500–4000 per cm		
	Thin Layer Chromatography	Stationary Phase (thickness)	Silica gel/TLC cards (0.2 mm)		
		Dissolution-diffusion agent	Butanol, Ethanol, Water (5:0.5:1.5)		
	High Performance Thin Layer Chromatography	HPTLC plate	HPTLC silica gel plate 60		
		Developing chamber	CAMAG horizontal developing chamber		
		Sample application	CAMAG Linomat IV		
		Scanner	CAMAG TLC Scanner		
		Data recording	CAMAG winCATS software		
Koenig et al. (2014)	TDS3 Thermal Desorption unit attached to Agilent 6890N-MSD 5973N Gas Chromatograph Mass Spectroscope	Thermal desorption temperature	90°C - 200°C	5mm × 1mm ballpoint pen ink line on 80GSM white sheet	2-phenoxyethanol (PE)
		Derivatization rate	up to 98.7 ± 0.3%		
		GC Column (Size of column)	NA		
		Carrier gas (flow rate)	Helium (1.2ml/min)		
		Min. – Max. Oven temp.	45°C - 270°C		
Koenig et al. (2015)	Agilent 6890 Gas Chromatograph - 5790 C Mass Spectrometer	GC Column (Size of column)	HP5-MS (30m × 0.25mm, 0.25µm)	1cm Ballpoint pen ink line on 80 GSM white sheet extracted in 15 µl chloroform containing PE-D_2	Solvents
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	50°C - 300°C		
Roman et al. (2015)	Multiple Headspace Solid Phase Micro-extraction Agilent 6890 Gas Chromatograph 5973-N Mass Spectroscope	SPME fibres	SPME fibres coated with 65 µm polydimethylsiloxane-divinylbenzene	Variable number of 1.20 mm discs of Black and blue ballpoint entries on a white paper extracted at 90 °C for 15 mins.	Volatile solvents
		Desorption time	1 min		
		GC Column (Size of column)	DB-1 Capillary column (30m × 0.25mm, 0.25µm)		
		Carrier gas (flow rate)	Helium (1.3ml/min)		
		Min. – Max. Oven temp.	55°C - 250°C		

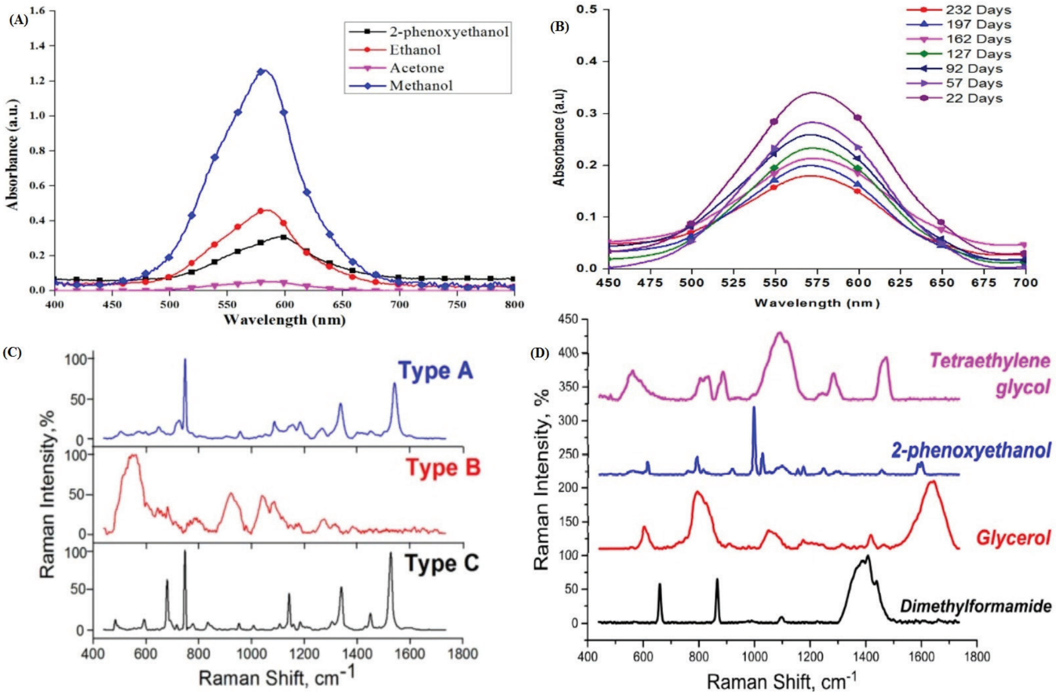

Figure 6- *(A) UV–Vis Spectra of blue ink extracted by using different solvents [31]. (B) Relationship between absorption of dye and time of writing in days [31]. (C) Raman spectra of three kinds of blue writing ink using 785 nm laser [30]. (D) Raman spectra of pure solvents using 785 nm laser [33].*

nique was fruitful only for blue ballpoint pens over a period of one year. Multiple regression models and analysis of variance (ANOVA) were applied to find out statistically significant organic compounds. PE, BZA, and MVBB were statistically significant and helped in analysing the age of ink [32]. The application of more than one method and comparison of their results was necessary to determine the age of ink.

Seven parameters used for dating of ink were calculated and compared over a period of one year by Koenig and Weyermann [34]. In continuation to their work, Koenig and Weyermann [35] tested three interpretation models, namely, the threshold method, trends approach, and calculation of likelihood ratio, using different aging parameters that gave promising results in the previous study, including, the quantity of phenoxyethanol, the difference between the quantities of PE for naturally and artificially aged samples (RNORM), and solvent loss ratio (R%). The initial concentration of PE and R% varied with the ink composition. Higher concentration of PE suggested younger inks and the decrease in the quantity of PE was rapid with time. However, lower concentration of PE was not a definite reminiscent of older inks. Higher concentration of R% suggested younger inks but not vice versa. R% values showed more variation than PE, although both parameters showed a correlation. The RNORM decreased with the increase in time, although it was distinct from R% values. RNORM and PE also showed a correlation. The natural solvent loss ratio (NR%) values were not significant over a one-week-old sample and correlations were not found with other parameters. The difference between the quantities of PE for naturally aged samples (NRNORM) values and RPA showed variability in results and gave results only for young ink samples. The implementation of alternative solvent loss ratio (R%*) was complicated and it did not offer any significant results as compared to R% [34].

Threshold values were specified for particular aging parameters under specific aging conditions. As there were chances of errors, optimisation of threshold values was necessary. Trend tests were based on the kinetics of ink aging and required multiple ink analysis. Trend tests were unsuccessful with PE, RNORM and R% due to higher variability and were not recommended without prior test on large samples of ink. Calculation of likelihood ratio considered the possibility of the document to be fraudulent and the possibility of the document to be authentic. Hence, a document could be categorised as young, old, or inconsistent. Large amount of PE could be concluded as a young ink sample. Nevertheless, small amounts of PE were not conclusive for older ink samples. Likelihood ratio for R% was least conclusive and prone to errors. Likelihood ratio for RNORM furnished best results without errors and proved to be the best technique for the determination of age of ink [35].

Andrasko and Lagesson-Andrasko [36] analysed the kinetics of phenoxyethanol by following two different methods for exposing the samples to various temperatures. In the first method, the injector temperature was raised from 100°C to 150°C to 200°C and finally to 225°C at an interval of 4 minutes each. In the second method the injector temperature was raised from 100°C to 200°C at an interval of 6 minutes. EL-Sabbah et al. [37] analysed phenoxyethanol present in pen inks which were aged naturally up to 3 years, which were either exposed to natural environmental conditions or stored in closed conditions, and samples aged artificially at 24°C and 70°C for 1 hour. Fig. 7 In order to establish a relationship between natural and artificial aging, Ortiz-Herrero et al. [38] analysed samples that were exposed to xenon lamp in SolarBox 1500e RH up to 257 hours. Various statistical parameters were also tested to validate the PLS model. Sauzier et al. [39] utilised visible spectroscopy to analyse pen ink writings up to 32 months stored in three different environmental conditions, that is, exposed to light, in the dark but exposed to air, and in the dark without exposure to air.

The initial peak of PE was sharp and was dependent on the rate of increase of temperature. Desorption of PE decreased with time. However, an increase was observed in the relative amount of PE at higher temperatures. Rapid decrease in the amount of PE was observed in fresh samples [36-37, 39]. Docucenter and spectroscopic method did not give positive results for determining the age of pen inks [37]. On spectral analysis, the distinctive near infrared (NIR) and UV-visible bands were identified, which accounted to the different rate and mechanism of degradation of fresh and old ink samples. Correlation between 143 hours of natural aging corresponded to 1 hour of artificial aging [38]. Certain factors like storage conditions, humidity, temperature, and initial composition of ink affected the results [31, 39].

Islek et al. [40] discussed a case for the analysis of the age of ink for a bond written with a ballpoint pen. The date of payment was different from the date of production of the bond, which raised suspicion that the dates were changed on purpose. The samples were drawn from the handwriting and signature on the bond. Plot was generated for both the samples, and the peak areas were obtained. The data was used to calculate the ratios which were different for both samples. Hence, it was concluded that the pen ink entries were made on different time intervals. Islek et al. [41] discussed another case from 2017, which required dating a part of a document made in 1996. It was asked to infer whether the ballpoint pen ink writing of that part of the document was made within the past two years or earlier. Plots were generated and retention time and peak areas of various dyes were evaluated. The values obtained for the questioned part of the document were different from the rest of the document, suggesting different age of writing. Relative ratio (V%) values were calculated, and a graph was plotted as a function of time, which suggested that the questioned part was 6-8 month old. The large time gap in the production of two writings was helpful in solving this problem. The specifications of instrument, sampling details and component studied are mentioned in Table 4.

2.2 Determination of age of non-ballpoint pen inks (Gel pens/Roller ball pens/ Fountain pens/ Iron gall pens)

2.2.1 Studies from the year 2006 to 2010

High performance liquid chromatography was the most used technique in this time frame followed by gas chromatography and UV-visible spectroscopy to analyse dye components of pen ink. Liu et al. [42] classified gel pens on the basis of solubility test using methanol. Dye based pens were further classified on the basis of the number of peaks of the

Table 4- *Ink dating studies on ballpoint pen from the year 2016 to 2020.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Freidenfelds et al. (2016)	SPME- Shimadzu GC-2010 Shimadzu GCMS-QP 2010 detector	GC Column (Size of column)	Restek RTX® 1MS (30m × 0.25mm, 0.25μm)		Volatile solvents and dye components
		Carrier gas (flow rate)	Helium (113.7ml/min)		
		Min. – Max. Oven temp.	40°C - 270°C		
	Waters Alliance 2695 with Waters Quatro-MicroTM API	HPLC Column (Size of column)	Waters Symmetry® C18 (4.6mm × 150mm, 5 μm)		
		Detector	MassLynx		
		Mobile phase	0.01% formic acid (pH 3) and Bacetonitrile (1:1)		
Gorshkova et al. (2016)	Thin Layer Chromatograph (TLC)	Stationary Phase	Silufol (PTSH-AF-15×15) on aluminium	1cm ballpoint pen ink stroke on paper extracted in the 2 ml DMFA for 2 hours at room temperature	Dye and pigment components
		Mobile Phase	Ethyl acetate: Isopropyl alcohol: Water: Acetic acid (30:15:10:1)		
	Senterra Raman spectrometer equipped with a laser module confocal microscope	Laser wavelengths	488, 532, 785 nm		
		Spectral recorder	Fibre optic sensor		
		Atomic absorption recording spectrometer	Dual-beam scanning spectrophotometer lambda 1050 with double monochromator		
	Chromatec-Crystal 5000.2 chromatograph equipped with flame ionization detector	NA			

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Sharma et al. (2017)	Shimadzu UV–2550 series Spectrophotometer	Wavelength	200-800 nm	5cm blue ballpoint pen ink extracted overnight using 10ml ethanol.	Dyes and solvents
Díaz-Santana et al. (2017)	Agilent Technologies 6850N/5975C gas chromatograph equipped with deconvolution reporting A.0400 and NIST v.2.0. Mass Spectral Library-AMDIS	GC Column (Size of column)	DB-5MS (30m × 0.25mm, 0.25μm) and VF-WAXms (30m × 0.25mm, 0.25μm) capillary columns	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-methylphenol)	Solvent and Dye components
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	45°C - 230°C		
	Agilent series 1260 Infinity HPLC system equipped with DAD Detector	HPLC Column (Size of column)	Agilent ZORBAX SBAq column (10 mm × 3.0mm, 3.5μm)		
		Mobile phase	Ammonium formate buffer (pH 4.0) in water and acetonitrile		
Grechukha et al. (2017)	SenterraRaman spectrometer equipped with a laser module confocal microscope	Laser wavelengths	488, 532, 785 nm	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
		Spectral recorder	Fibre optic sensor		
		Atomic absorption recording spectrometer	Dual-beam scanning spectrophotometer lambda 1050 with double monochromator		
	Chromatec-Crystal 5000.2 chromatograph equipped with flame ionization detector	NA			
Ortiz-Herrero et al. (2018)	Cary 5000 UV–vis-NIR spectrophotometer coupled with DRA-CA-5500 integrating sphere	Wavelength	200-2500nm	1 cm diameter ink sample on spread 80 GSM white sheet using brush.	Dye components and volatile components
		Speed	600 nm/min		
	Waters™ 2690 separations Module	HPLC Column (Size of column)	Waters™ Atlantis dC18 (100 ×3.9 mm, 3 μm)	0.1 mg of fresh ink/ 7 punches of artificially aged ink extracted in 1ml MeOH	
		Detector	Waters™ 996 PDA detector		
		Mobile phase	NA		
Koenig et al. (2018)	Agilent 6890 Gas Chromatograph - 5790 C Mass Spectrometer	GC Column (Size of column)	HP5-MS (30m × 0.25mm, 0.25μm)	1cm Ballpoint pen ink line on 80 GSM white sheet extracted in 15 μl chloroform containing PE-D_2	Solvent and Dye components
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	50°C - 300°C		

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Isleket al. (2018)	Thermo Scientific DegazerSystem SCM 1000 with Pump Spectra System P1000	HPLC Column (Size of column)	Phenomenex Onyx C18 Monolitic Column (100 × 4.6 mm)	Ballpoint pen ink entries extracted in 100 µl of methanol	Dye components
		Detector	UV detector 1000 system		
		Mobile phase	0.05M Phosphate buffer, 100% Methanol and 100% Acetonitrile (50:30:20)		
Sauzier et al. (2018)	4000 UV-Visible Spectrophotometer with DRA-900 Internal Diffuse Reflectance	Operating setup	Double beam mode with reduced slit height	25 mm^2 ballpoint pen ink entries on white sheets	Dye components
		Data Acquisition	Cary WinUV Bio Version v. 4.20		
		Wavelength, Speed	400–700 nm, 600 nm/min		
		Data pre-processing and analysis software	Unscrambler® X 10.4 software		
Andrasko et al. (2018)	Agilent 6890 gas chromatograph equipped with a 5973 series mass selective detector	GC Column (Size of column)	DB 5 capillary column (30m × 0.25µm, 0.25µm)	0.3–0.4 mm ballpoint pen ink line on 80 GSM white sheets.	2-phenoxyethanol
		Carrier gas (flow rate)	Helium (10 psi)		
		Min. – Max. Oven temp.	100°C - 240°C		
EL-Sabbah et al. (2019)	Agilent 6890 gas chromatograph equipped with an Agilent mass spectrometric detector	GC Column (Size of column)	HP-5MS fused silica capillary column (30m × 320µm, 0.25µm)	1 cm ballpoint pen ink entry on 80 GSM A4 white sheets extracted with 10ml carbon tetrachloride with acetonitrile (weak) and 10 ml chloroform with acetonitrile (strong)	2-phenoxyethanol
Islek et al. (2020)	Thermo Scientific Degasser System SCM 1000, Pump Spectra System P1000	HPLC Column (Size of column)	Phenomenex Onyx C18 Monolithic Column (100 × 4.6 mm)	1.2 mm ink entry extracted in methanol	Crystal violet and phenoxyethanol
		Detector	UV detector 1000 system		
		Mobile phase	0.05M phosphate buffer (pH = 3), 100% methanol, 100% acetonitrile (50:30:20)		
	Unity Thermal Desorber Agilent HP 6890N GC 5975B MS	GC Column (Size of column)	DBVR-X (60 m × 0.25mm, 1.4µm)		
		Thermal desorption temperature	90°C to -10°C to 300°C		
		Min. – Max. Oven temp.	45°C - 200°C		
		Ionisation level	70eV		

Table 5- *Ink dating studies on non ballpoint pen from the year 2006 to 2010.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Liu et al. (2006)	Ion-Pairing High-Performance Liquid Chromatograph	HPLC Column (Size of column)	Luna C18 column (250mm × 4.60mm, 5μm)	5cm black gel pen ink line extracted in 0.5 mL 40 mmol/L tetrabutylammonium bromide buffer: acetonitrile (v/v = 1:1)	Dye components
		Detector	Waters 490E programmable multi wavelength UV detector		
		Mobile phase	20μl tetrabutylammonium bromide (pH 7.0) and Acetonitrile (40:60)		
Xu et al. (2006)	Hewlett-Packand Model 6890 gas chromatography equipped with flame ionization detector	GC Column (Size of column)	DB-FFAP (30m × 320 μm, 0.25μm)	2 cm pen ink line extracted by 1ml methanol containing ethyl benzoate	Dye components
		Carrier gas (flow rate)	Nitrogen (2.5ml/min)		
		Min. – Max. Oven temp.	60°C - 220°C		
	Shimadzu 250 UV-VIS Spectrophotometer	NA	NA		
Liu et al. (2006)	Waters 510 Pump	HPLC Column (Size of column)	Luna C18 column (250mm × 4.60mm, 5μm)	5cm blue gel pen ink line extracted in 0.5 ml 10 mmol/l tributylamine acetate buffer: acetonitrile (v/v = 1:1)	Dye components
		Detector	Waters 490E programmable multi wavelength UV detector		
		Mobile phase	20μl tributylamine acetate (pH 7.0) and Aacetonitrile (40:60)		
	ACQUITY ultra performance liquid chromatography	HPLC Column (Size of column)	Bridged Ethane Hybrid Column (50 mm × 2.10 mm, 1.7 μm)		
		Detector	Waters Quattro Premier XE Mass Spectrometer		
Wang et al. (2008)	Ion-Pairing High-Performance Liquid Chromatograph	HPLC Column (Size of column)	Inertsil C18 (250mm × 4.60mm, 5μm)	2.5cm fountain pen ink line extracted by tetrabutylammonium bromide buffer, acetonitrile (1:1)	Dye components
		Detector	Schnell ScannendesSpektralphotometer K-2600 UV detector		
		Mobile phase	40 mmol/L TBABr buffer (pH 7.0) with acetonitrile (50:50 (v/v))		

main dye component and their retention time. Fig. 7 The relative peak height of naturally aged and artificially aged samples was calculated. Xu et al. [43] analysed naturally aged and artificially aged pen inks and calculated the ratio of difference between the heated and unheated samples (D%). Liu et al. [44] classified gel pens on the basis of solubility test using ethanol. Wang et al. [45] worked on the identification and dating of fountain pen inks. The ink components were separated and were identified on the basis of the number of major components. The change in the relative peak height of each component was studied to determine the age of pen inks.

The relative peak height decreased with time and

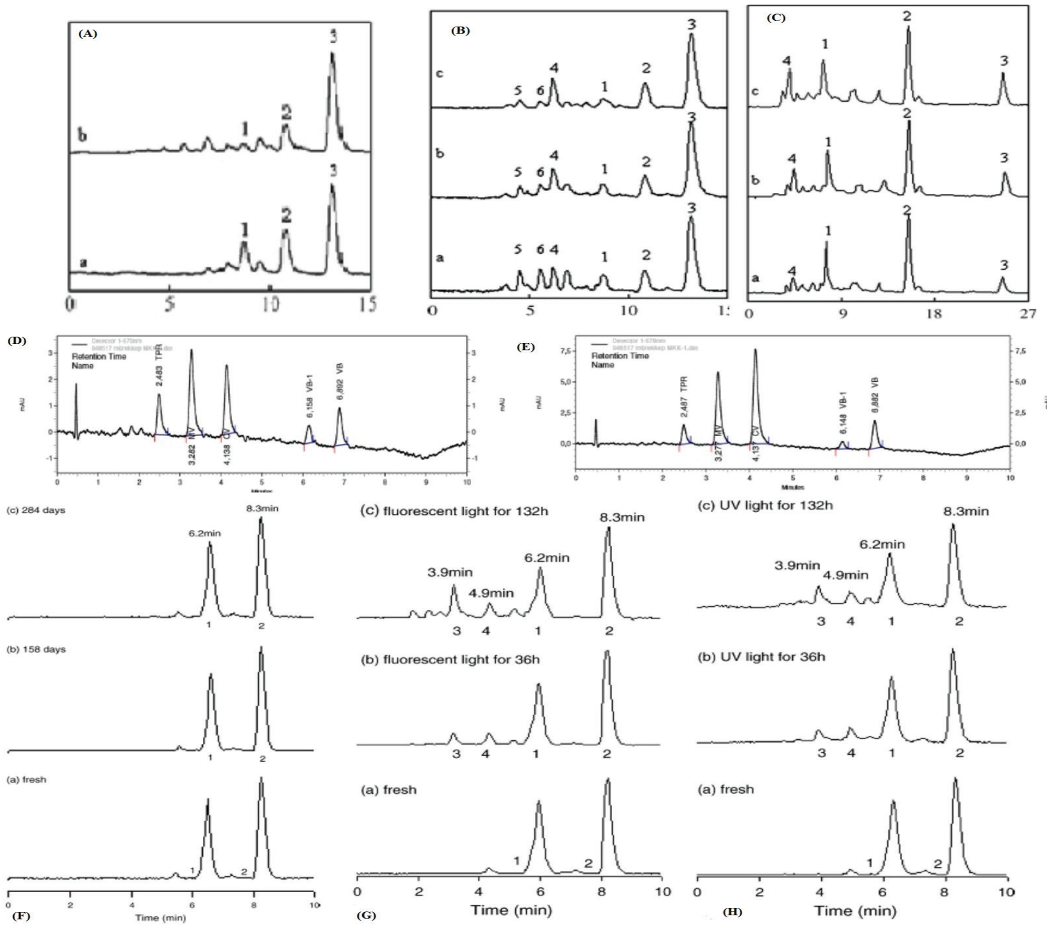

Figure 7- *Chromatograms of ink entries on paper (A) after exposure to UV lights for (a) 0 h, and (b) 156 hours [42]; (B) Stored in natural condition for (a) 7 days, (b) 202 days, and (c) 385 days [42]; (C) Exposed to fluorescent lamp for (a) 0 h, (b) 72 h, and (c) 156 hours [42]; (D) Taken from the signature portion of the sample [38]; (E) Taken from the address portion of the sample [38]; (F) Under natural conditions [44]; (G) Under fluorescent light [44]; (H) Under UV light [44].*

subsequently the relative peak heights of new components increased in both naturally aged and artificially aged samples [42-45]. A large decrease in peak height was noted within one hour. D% value between 30 and 80 suggested a fresh sample that is written within ten days. D% value between 0 and 30 suggested samples written between ten to ninety days. D% value equal to 0 suggested old sample, that is, written before ninety days [43]; Fig. 7. The changes in composition of the dye components and the degradation products were related linearly to the natural and artificial conditions [44-45]. The conditions of writing and storing cannot be replicated and hence, they posed a drawback for relative aging [43]. The specifications of instrument, sampling details and component studied are mentioned in Table 5.

2.2.2 Studies from the year 2011 to 2015

Thin layer chromatography was the most used technique followed by high performance liquid chromatography, laser desorption ionization, gas chromatography and microscopy to analyse dye and solvent components of pen ink. Wu et al. [46] analysed gel pen inks and categorised them depending on the presence of surfactants. Fig. 8 The ink samples were further distinguished on the basis of their mass number or the mass by charge ratio. The pre-

Table 6- *Ink dating studies on non ballpoint pen from the year 2011 to 2015.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Wu et al. (2012)	Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer	Laser	337 nm nitrogen laser in positive or negative modes	5cm gel pen ink line sample extracted Dimethyl formamide (DMF) for 12 h	Dye components
		Ion Source	IS1- 19 kV and IS2 - 15.7 kV		
	High Performance Liquid Chromatography Quadruple-Time of Flight-Mass Spectrometer	HPLC Column (Size of column)	Agilent ZORBAX SB-C18 (2.1 × 150 mm, 5μm)		
		Detector	microTOF-Q II Mass Spectrometer		
		Mobile phase	20 mmol/L Ammonium bicarbonate with Acetonitrile		
Li et al. (2014)	Motic-microscope equipped with Reflective Light Source	Imaging Software	Motic Images Advanced 3.2	1cm Black Gel pen ink lines on three kinds of paper extracted with DMF, Dioxane and Ether (3:7:14) for 1 min.	Dye components/ entire ink
		Magnification	20×		
		Gray scale measuring	Adobe Photoshop7.0.1		
	Thin Layer Chromatography	Stationary Phase	Silica gel GF254		
		Dissolution-diffusion agent	Mixture of DMF (2ml), Anhydrous Ethanol (13ml) and TiO power (13g)		
Li et al. (2014)	Agilent gas chromatograph equipped with a flame ionization detector	GC Column (Size of column)	DB-FFAP (30m × 320μm, 0.25μm)	20 × 1mm black gel pen ink line extracted in 10 μl methanol containing ethyl benzoate.	Volatile solvents
		Carrier gas (flow rate)	Nitrogen (2 ml/min), Hydrogen (40 ml/min), Air (300 ml/min)		
		Min. – Max. Oven temp.	333.15 K - 493.15 K		
Li et al. (2015)	Motic microscope	Imaging Software	Motic Images Advanced 3.2 software	1cm pen ink line extracted in a solution of butanone, ether, and 5% oxalic acid (10:8:19). Samples were directly analysed under microscope using the dissolution diffusion agent (2ml DMF, 7ml surface active agent, 13ml anhydrous ethanol, and 13g TiO power)	
		Light source	Reflective light source		
		Magnification	20×		
		Other Software	Adobe Photoshop7.0.1 software		
	Thin Layer Chromatography	Stationary Phase	Qingdao marine Silica gel GF254 plate		

cursor ions were studied along with parent ions to positively identify dye components of various inks. Li et al. [47] classified gel pen inks on the basis of the number of peaks and their retention time. Fig. 9 & 10 Li [48] worked on the dissolution-diffusion method to differentiate black gel pens on the basis of dye composition and to study the aging of ink. The gel pen inks were differentiated into four differ-

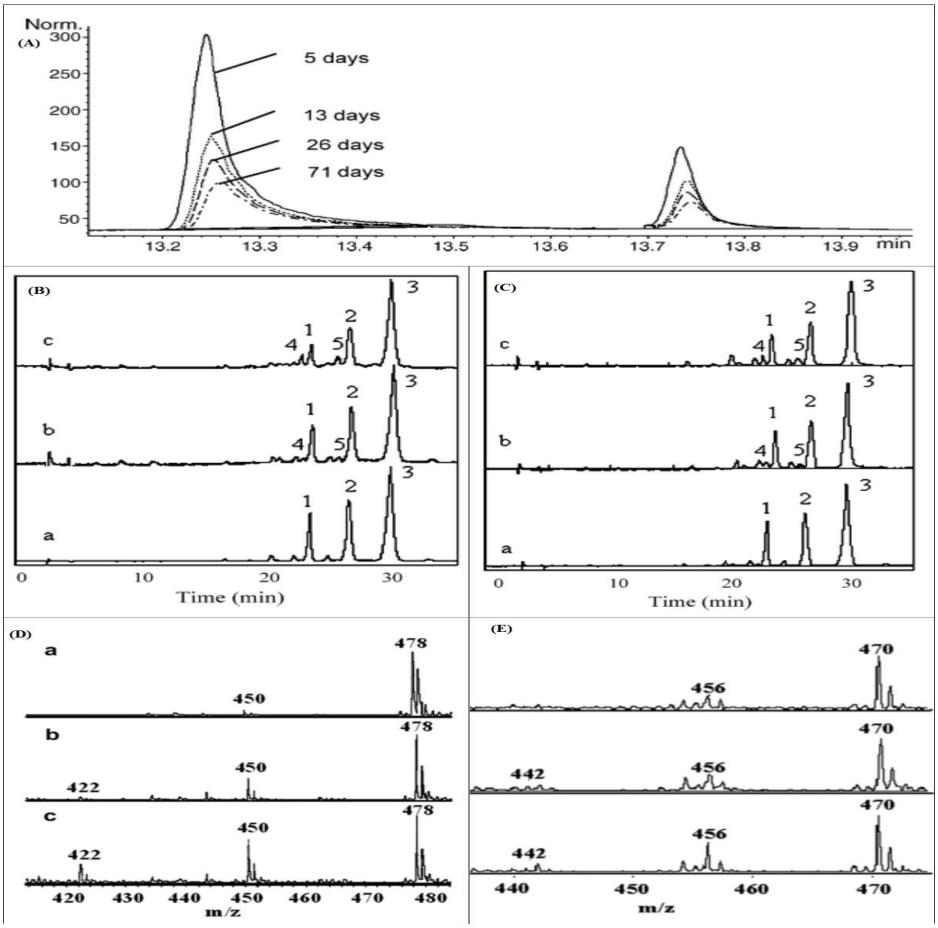

Figure 8- *(A) Decrease in chromatographic peaks with increasing time [43]. HPLC chromatograms of ink entries on paper aged under (B) natural conditions [45] and (C) UV illumination [45]. LDI-MS spectra of gel pen ink entries before and after exposure to (D) UV light for (a) 0 h, (b) 162 h, and (c) 354 hours [46] and (E) Natural conditions for (a) 0 day, (b) 585 days, and (c) 1080 days [46].*

ent categories on the basis of number, colour, and radius of spot rings on thin layer chromatography (TLC) Fig. 3 & 11 plates. Fig. 3 Li and Xie [49] analysed iron gall inks using dissolution-diffusion method up to 20 months. Fig. 9 & 10.

The relative intensities of dye components decreased with time and the relative intensities of the degradation products increased, respectively. In natural aging conditions, the degradation was relatively slower than artificial conditions [46-47]. Different solvents evaporated at different rates due to the difference in their boiling point. A relationship can be acquired between natural aging and artificial aging [47]. The larger value of rate of dissolution-diffusion corresponded to less age of ink, while the smaller value of rate of dissolution-diffusion corresponded to more age of ink [48]. Difference in proportion of ink components, type of substrate, thickness of ink stroke and storage conditions affected the rate of dissolution-diffusion [48-49]. The specifications of instrument, sampling details and component studied are mentioned in Table 6.

2.2.3 Studies from the year 2016 to 2020

Gas chromatography (GC) was the most used technique in this time frame followed by liquid chromatography (LC) and Raman spectroscopy to analyse solvent components of pen ink. Sun et al. [50] executed identification and dating of gel pen

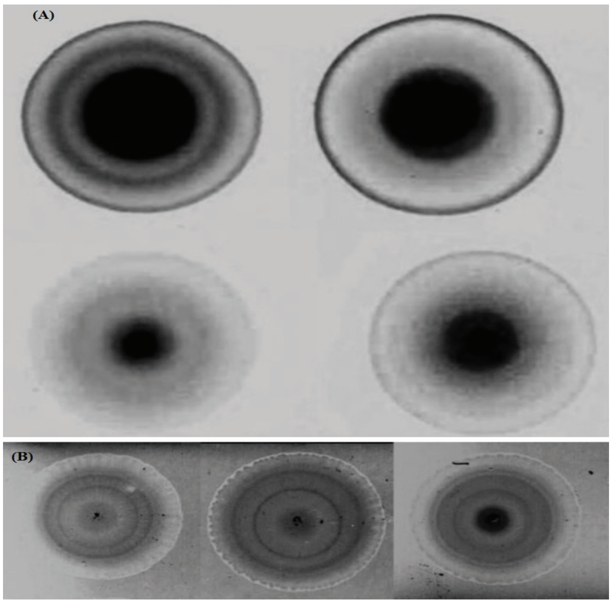

Figure 9- *TLC diagram of (A) Four types of gel inks [47]. (B) Three types of iron gall inks [49].*

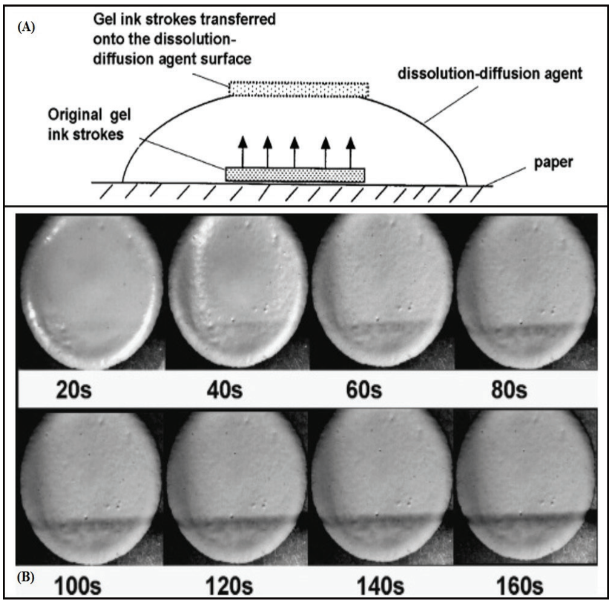

Figure 10- *(A) The schematic diagram of dissolution–diffusion process [47]. (B) Photographs of dissolution-diffusion process at various time intervals [49].*

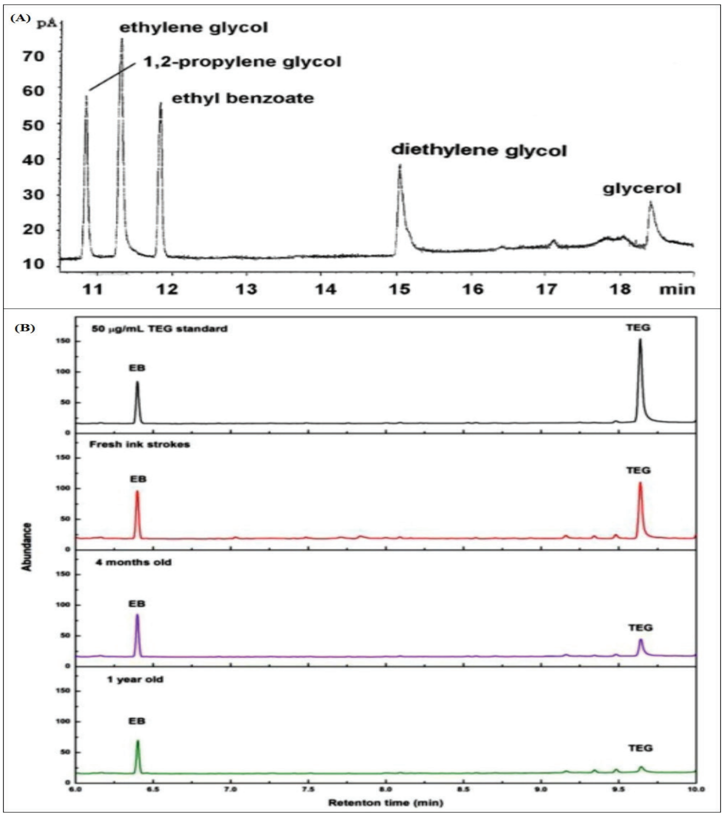

Figure 11- *Gas chromatogram of (A) Four pure volatile solvent components and internal standard (Ethyl benzoate) [48]. (B) Standard triethylene glycol, fresh ink strokes, 4 months old ink sample and 1 year old ink sample [52].*

inks containing polyethylene glycol (PEG) oligomers. Gel pens were differentiated on the basis of the mass by charge ratio (m/z) of oligomeric PEG. Aginsky [51] analysed a decrease in the contents of 2-pyrrolidone (2-PD) solvent present in the Pilot® roller-ball pen inks stored in natural environmental conditions. Ni et al. [52] analysed the aging of triethylene glycol (TEG) in carbon-based gel pen inks. On the basis of the quantity of TEG, the pens were classified into three groups as high, medium, and low. Loss of TEG with time accounted for the aging of ink samples; Fig. 11.

Classification based on liquid chromatography high resolution mass spectrometry (LC–HRMS) was better than Raman spectroscopy. PEG oligomers degraded with time as shift in the mass by charge ratio was noted. Low molecular weight oligomers showed an increase in their relative quantity with the increase in time. Degradation of PEG oligomers was comparatively slower in naturally aged samples as compared with artificially aged samples [50]. For all types of papers and inks the contents of 2-PD were completely lost with time, except the inks containing non-volatile binders. These binders retained a constant amount of solvent after many years of aging. The thickness of the ink layer at the point of intersection was double than that of a single stroke and the aging curves showed that the ink solvent took approximately twice the time to degrade as of the thinner ink layer. Similar results were seen for the samples analysed from the proximity of the ink stroke [51]. Storage condition and solvent diffusion affected the process. The rate of degradation was rapid initially and then the process slowed, till the curve straightened [51-52].

Rahiche et al. [53] employed multispectral imaging for dating historical documents produced using iron gall ink from the 17th- 20th century. The original documents were digitised using a multispectral imaging system and eight images were made for each document at different wavelengths of light. Features extracted using visible light had less discrimination power as compared to the features extracted using UV and IR light. Further analysis was done on features extracted using UV and IR light. Algorithm based on kernel discriminant learning for ordinal regression technique was used for ordinal classification. Most documents were classified correctly, and distinguishing was possible up to year level [53]. The specifications of instrument, sampling details and component studied are mentioned in Table 7.

2.3 Determination of age of stamp pad/seal inks

2.3.1 Studies from the year 2009 to 2014

Gas chromatography (GC) was the most used technique in this time frame followed by high performance liquid chromatography (HPLC), UV spectroscopy and thin layer chromatography (TLC) to analyse dye and solvent components of stamp inks. Yao et al. [54] studied the aging of stamp inks aged in natural and artificial conditions. The dye components and the volatile components of these ink samples were separated. Further, these components were used to identify and categorise the ink samples. One or two major components and few trace components were detected for all ink samples. The inks were categorised into groups and subgroups on the basis of the number of peaks and their retention time. Few inks showed variation in the retention time of their major and trace components and thus were individualised. In 2014, Li et al. analysed ink-pad seal inks of red colour using four types of paper and stored under controlled conditions. The samples were extracted and analysed using thin layer chromatography. Cyclohexane was selected as a weak extraction solvent, while chlorobenzene was selected as a strong extraction solvent. Standard deviation and maximum deviation were calculated

Table 7- *Ink dating studies on non ballpoint pen from the year 2016 to 2020.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Sun et al. (2017)	Renishaw Raman spectrometer	Laser wavelength	785nm	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
		Grating	1200 rulings/mm grating		
		Integration time	10 second		
	Thermo Fisher Scientific UltiMate 3000 UHPLC and a Q Exactive ™ Orbitrap mass spectrometer	HPLC Column (Size of column)	Agilent Zorbax SB C18 column (150 × 2.1 mm, 5 µm)		
		Sheath gas	Nitrogen		
		HRMS Scanning Range	From m/z 100 to 1500		
		Software	Thermo Xcalibur 3.0 software		
Aginsky (2017)	Agilent 6850 gas chromatograph interfaced with an Agilent 5975C mass selective detector	GC Column (Size of column)	DB-5MS (30m × 0.25mm, 0.25µm) cross linked column	3 × 0.5 mm discs of ink on various type of papers extracted in 2 µl chloroform containing (up to 0.2 ng/µl) deuterated phenoxyethanol (internal standard)	2-pyrrolidone
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	36°C - 270°C		
Ni et al. (2020)	Thermo Fisher Scientific Trace 1300-ISQ Gas Chromatograph Mass Spectrometer	GC Column (Size of column)	HP-INNOWAX column (30 m × 0.25mm, 0.25µm)	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)
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	80°C - 260°C		
	Agilent 7890A GC system equipped with a flame ionization detector (FID)	GC Column (Size of column)	DB-FFAP (J&W 122-3232) column (30 m × 0.25mm, 0.25µm)		
		Carrier gas (flow rate)	Nitrogen (2ml/min)		
		Min. – Max. Oven temp.	60°C - 225°C		
		FID Temperature	280°C		
Rahiche et al. (2020)	MS imaging system	Camera	Kodak Monochrome CCD Chroma X3 AF 6303E	NA	NA
		Resolution	3072 × 2048 pixels		
		Filter	Set of 8 chromatic filters		

to analyse errors in the data. In 2014, Li analysed stamp pad inks on three different types of paper. Stamp pad inks were classified into 5 groups on the basis of the composition of the volatile solvent. Aging parameters were determined using the ratios of peak area of volatile components of the ink and the internal standards. Standard deviation, maximum deviation and relative standard deviation were calculated to analyse errors in the data.

Three common dyes were identified, namely, the bronze red c, scarlet powder and pigment fast red r. On the basis of the mass spectra, the inks were divided into 5 primary groups and further into secondary groups depending on the number and type of components. This multi-level examination helped in the identification of the ink entries, which could not have been possible otherwise. The rate of degradation was dependent on the chemical structure of the dye component, additives, and condition of ageing. The rate of degradation of volatile components was higher in the first 3-4 months [54]. The rate of extraction was fast in the first 3 months which eventually slowed down and was negligible after 5 months. Different brands of inks and the type of paper influenced the rate of extraction. The method was useful for dating inkpad inks for up to 6 months [55]. No effect of the type of paper was observed on the aging of ink in this method. The samples aged under UV light, temperature, and humidity also showed similar results and a correlation was also drawn [56]. The volatile components in the ink decreased with increase in time. The plot can be divided into three parts. In the first part, the volatile components decreased rapidly, in the second part the decrease is slow and in the third part there is negligible change [55-56]. The specifications of instrument, sampling details and component studied are mentioned in Table 8.

2.3.2 Studies from the year 2015 to 2019

In 2019, Ouyang et al. differentiated stamp pad inks using a UV visible spectrophotometer. Visual spectrum comparator 6000 was used to study the luminescence of paper and spectra of paper were collected using a Fourier transform infrared spectrometer. Stamp pad inks were applied on different types of paper. Stamp pad inks were differentiated into 4 classes on the basis of the area, position, and height of absorbance peaks. No interference of paper was observed in the peaks. Rate of extraction method was used to establish a correlation between the age of ink and the absorbance ratio. Stamp pad inks were dissolved in extraction solvent and UV visible spectra were generated, so as to calculate the absorbance ratio. The age of ink was inversely proportional to the absorbance ratio. Different brands of stamp pad inks had different absorbance ratios. The type of paper also demonstrated influence on the absorbance ratio. It was suggested to conduct further work on the absorbance ratio method for the determination of age of ink [57]. The specifications of instrument, sampling details and component studied are mentioned in Table 8.

3. Discussion

In the time span from the year 2000 to the year 2020, major research was done on ballpoint pen inks only. Various researchers have given their inputs according to their research work. Ink does not age inside a cartridge. However, without using a pen over prolonged storage, it could result in aging of ink at the tip of the pen [13]. The process of evaporation is rapid and depends on the quality of paper used [12]. Solvent system disappears rapidly after the ink has been applied on the paper due to evaporation and diffusion. Determining the precise age is difficult, however establishing of age limits can be performed [15]. It is difficult to produce samples

Table 8- *Ink dating studies on stamp pad inks from the year 2009 to 2019.*

Author (Year)	Instrument used	Specification of Instrument		Samples	Component studied
Yao et al. (2009)	Ion-Pairing High-Performance Liquid Chromatograph	HPLC Column (Size of column)	Luna C18 column (250mm × 4.60mm, 5µm)	1cm stamp ink line samples extracted by Dimethyl formamide (DMF)	Dye components and volatile solvents.
		Detector	Multi-wavelength UV detector		
		Mobile phase	20 mmol/L TBABr buffer (pH 7.0) with Acetonitrile		
	Thermo-Fisher Trace Gas Chromatograph Mass Spectrometer	GC Column (Size of column)	DB-5MS fused-silica capillary column (30m × 0.25mm, 0.25 µm)		
		Carrier gas (flow rate)	Helium (1ml/min)		
		Min. – Max. Oven temp.	100°C - 290°C		
Li et al. (2014)	Thin layer chromatography	Scanner	CAMAG TLC scanner 3	10 × 1 mm diameter discs of stamp pad ink was extracted in cyclohexane for 1 minute and chlorobenzene for 15 minutes.	-
		Software	WINCATS software		
		Stationary Phase	Silica gel plate		
Li (2014)	Agilent 6890 G1530N gas chromatograph equipped with Agilent flame ionization detector	GC Column (Size of column)	DB-FFAP (30m × 320µm, 0.25µm)	30 × 1mm diameter discs of stamp pad ink was extracted in 5µl ethyl benzoate (1µl) diluted in 100 ml ethanol.	Volatile solvent
		Carrier gas (flow rate)	Nitrogen (1.5 ml/min), Hydrogen (40 ml/min), Air (300 ml/min)		
		Min. – Max. Oven temp.	60°C - 230°C		
Ouyang et al. (2019)	UV-2550 Ultraviolet visible spectrophotometer	Spectral bandwidth	2.0 nm	1cm Stamp pad ink line extracted in 2ml solution of dimethylformamide, n-butanol and methylene chloride (2:1:1)	Dye components
		Scanning wavelength	750–200 nm		
	Foster and Freeman visual spectrum comparator 6000	Excitation wavelength	485–590 nm (visible light) and 365 nm (long wavelength ultraviolet)		
		Integration time	250 ms		
		Receptive wavelength	645 nm and 695nm		
		Magnification	9.39		
	NICOLET 5700 micro-Fourier transform infrared spectrometer	Resolution	8 cm^{-1}		
		Spectral Range	650–4000 cm^{-1}		
		Number of scans	15		

to estimate the relative age as the circumstances of writing and storing cannot be replicated [15, 39, 43]. The storage history can be determined by the amount of degradation products based on the ternary diagrams [9]. However, in our opinion, it may not be true as the storage conditions are not constant for certain documents.

Ink aging is a complex process as many factors like the type of substrate, composition of ink, and storage conditions influence the process [14, 17-18, 22, 25-29, 31, 37-39, 42, 45-49, 52, 54, 57]. Thickness of ink entries also affects the process of aging [20]. Hence, it is difficult to compare artificially aged samples with the samples that aged in natural conditions [17, 28]. Exposure to light or heat changes the ink composition which leads to odd results for natural aging [10]. Li et al. [47] and Li [48] mentioned that natural aging, UV induced and heat induced aging are related and can be used to know whether a document was aged artificially.

Although the composition of pen inks varies among different makes and models, but the aging behaviour is similar [28, 54]. Sample extraction with a solvent may produce unwanted effects and hence samples must be examined directly from the paper. It is important to know the initial composition of ink sample to examine reproducibility of the test method [14]. Ageing of ink follows a complex pathway and validation of aging methods including inter laboratory analysis, error rates, and quantification of limits is necessary [1, 22]. Database shall be made for various ink samples [31].

A steadfast opinion can be formed only after examination of adequate sample size over sufficient time interval [11]. The interpretation of results should be logical and fact based [22]. According to Koenig et al. [26] calculation of RPA values and solvent loss ratio using RPA (R%*) proved to be the best methods to determine the age of inks. However, Koenig and Weyermann [34] reported that the quantity of phenoxyethanol (PE), the difference between the quantities of PE for naturally and artificially aged samples (RNORM), and solvent loss ratio (R%) methods gave promising results. Likelihood ratio approach proved to be the best model of interpretation [37].

Not many reliable methods are available for the purpose of determining the age of ink. Most researchers have focused on colorants or solvents present in the inks. Much work has been done on samples stored in controlled laboratory conditions only. Research related to normal storage conditions are required, which take into consideration the random exposures of samples to the day light and artificial light. Factors like type of substrate, thickness of ink entries, composition of ink, and storage conditions should be analysed prior to the dating of any ink sample. Not many methods were successful over a longer duration of time. Most of the methods gave best results only up to 6 months. Roman et al. [28], Ortiz-Herrero et al. [38], and Wu et al. [46], claimed to give aging results up to 5 years using DATINK method, DATUVINK method, and variations of its relative intensities, respectively. There is a need for the researchers to collaborate to develop a method which can be applied on all brands and types of inks. Various techniques could be clubbed and application of statistics and chemometrics could help. Multiple components of ink should be studied.

4. Conclusion

This review takes into account all the major works done so far on the determination of age of ink from the year 2000 to 2020. Various scientists have tried to work a lot on this issue, but no premier technique has been developed until now. Various analytical instruments have helped to draw certain conclusions. However, none of them is truly pleasing in terms of objective results and the reason for this is the complex degradation process of ink. Gas chromatography was the most widely used analytical instrument followed by high performance liquid chromatography and spectrometric techniques, in the case of dating of ballpoint pen inks. However, high performance liquid chromatography was more preferred than gas chromatography, in the case of dating of non-ballpoint pen inks.

Majority of the research work have been conducted on ballpoint pen inks only and a very few works related to non-ballpoint pen inks and stamp inks can be encountered. It is recommended to conduct research work on the printing inks and local brands of writing instruments. It is also suggested to carry out more extensive research work on all types of inks. The techniques should be less time consuming and economical. Various scientists throughout the world should collaborate to work on this issue to draw better conclusions.

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Conflict of interest

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