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Blue and Black Ballpoint Pen Inks: a Systematic Review for Ink Characterization and Dating Analysis

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Abstract. Documents are frequent targets of fraud and adulteration. Sometimes it is not enough to determine the document's authenticity or authorship, but it is also necessary to demonstrate when the document was signed or written. Determining the age of a document, also known as ink dating analysis, is still a challenge for the forensic examiners. There are two main approaches for the dating of ballpoint pen inks: the static method, which is based on the characterization and identification of the ink composition and comparison to a reference collection, and the dynamic method, which involves the study of ink's processes and alterations that occur with time, considering environmental aging factors such as light and humidity. This article aims to provide a comprehensive systematic review of the studies regarding ballpoint ink characterization and dating, in the last ten years. There are several methods, destructive and non-destructive, which are capable of characterizing and differentiating blue and black ballpoint pens that have shown applicability to the static approach. Regarding the dynamic dating methods, most studies quantified the loss of 2-phenoxyethanol (2-PE) solvent over time using GC-MS, or studied the dyes degradation through different methods. Although ink dating approaches offer relatively good accuracy, there is still more research to be done, such as the documents' storage conditions evaluation, the influence of initial ink quantity variation between different pen brands and writing fists, and the type of paper.

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Keywords: Ballpoint pens; Ink characterization; Ink dating analysis.

1. Introduction

The Forensic Documentoscopy aims to identify information regarding the document history, as well as its authenticity and the detection of a variety of alterations. With respect to the graphoscopic confrontation, sometimes it is not enough to determine only the document's authenticity and authorship, but it is also necessary to demonstrate the potential age of a document. Pen ink dating analysis can be instrumental in those instances, but still a challenging task for forensic scientists due to the variety of factors that can influence the analysis[1-3]. A document's dating analysis involves the chemical, optical and physical examination of ink and paper. This review will focus on approaches for ink analysis.

There are two major groups of writing instruments: the ballpoint pens, containing oil-based inks, and the non-ballpoint pens, which are water-based inks. Ballpoint pens are composed of dyes, vehicles, resins, and additives[1,4]. Dyes are responsible for imparting color to the ink. The vehicles are the substances responsible for the homogenization of the ink's compounds, primarily solvents. The resins confer viscosity, paper adherence, lubricant properties and durability to the ink. Finally, additives are compounds with specific characteristics, improving the ink's performance[1,4].

The ink dating of ballpoint pen inks is performed by two main approaches: the static method and the dynamic method[1,2,5]. The static profile is based on characterization or identification of the ink composition, which is often compared to other pen ink known sources. The dynamic one, however, involves the elucidation of ink's processes and changes that occur over time, as a result of ink interaction with environmental factors such as light and humidity.

In the static approach, inks of known manufacturing history are identified by visual, microscopic and chemical methods, and compared to the questioned ink. The static approach requires that the standard reference ink specimens are traceable with known manufacturer's information and date of the first production[6]. Since the static approach assumes the measured profiles of the ink have not changed over time, it is critical that the comparison standards are representative and stable. A superior accuracy in dating estimations is possible when more extensive and comprehensive ink collection sets are used. Likewise, the ink dating uncertainty improves when highly informative and discriminating analytical methods are used for examination.

Studies of the dating of writing inks have been reported since the 1960s when Hoffman began the first ink reference collection and characterized their profiles by ultraviolet fluorescence, near-infrared reflectance, luminescence and thin layer chromatography (TLC). In the early 1970s, Brunelle started one of the largest international writing ink libraries, first developed at the ATF and later maintained at the United States Secret Service (USSS). The inks were characterized by semi-quantitative TLC, HPLC, FTIR, and GC. In 2009, Neumann *et al*. developed an automated method to search and identify writing inks using high-performance thin layer liquid chromatography (HPTLC), mathematical algorithms and automated software. This project helped with the creation and standardization of the USSS Digital Ink Library and probabilistic interpretation models for the interpretation of ink evidence[7-10].

Regarding the dynamic profile, various studies have evaluated techniques to estimate how long the pen ink has been on paper, following these principles[1,11,12]: a) <u>dyes degradation</u>: dyes degrade under light exposition on the ink. On theory, it's possible to compare the intact dyes inside the pen cartridge, or recent writing, with dyes on the paper for some time, which suffered light exposition and degradation; b) <u>solvent evaporation</u>: since all pen inks contain volatile compounds, right after ink deposition on paper, those solvents begin to evaporate. This process does not occur inside the pen's cartridge. The solvent quantity decreases over time; c) <u>resin polymerization</u>: at the moment when the ink is on paper, its solubility begins to diminish, and with the time elapsing, it is more difficult to extract those compounds from the paper.

Briefly, once the ink is on paper, transformations begin to occur: the solvents evaporate, the dyes degrade, and the resins polymerize, until the moment when a balance is established and no more modification happens[1,4]. The dynamic ink dating analysis is based on the comparison between the intact ink, inside the pen cartridge or on recent application, with the ink placed on paper for some time[12]. Based on the transformations, it is possible to verify for how long the ink has been on paper[12,13]. There are three groups of instrumental methods for ink dating and analysis: the separation techniques, the mass spectrometry and the spectroscopy techniques[13].

Given the high judicial demands involving documents' age, this article aims to review the leading scientific publications regarding ballpoint ink characterization and dating, in the last ten years. This data can help forensic experts to improve their scientific reports, as well as can support new research in this area.

2. Methods

This systematic review was performed in August 2018 on the following databases: Google Scholar, Pubmed, Science Direct and Science.gov. The strategy for this research is presented in Figure 1. The descriptor used was "ballpoint pen inks". The inclusion criteria were: a) papers that studied blue and black ballpoint pen inks, for characterization or dating analysis; b) articles published in the last 10 years. Those criteria were chosen to review the most recent methods used for the most common pens used in all kind of documents.

The initial research identified 112 non-redundant papers publications, and 63 of those fit the inclusion criteria.

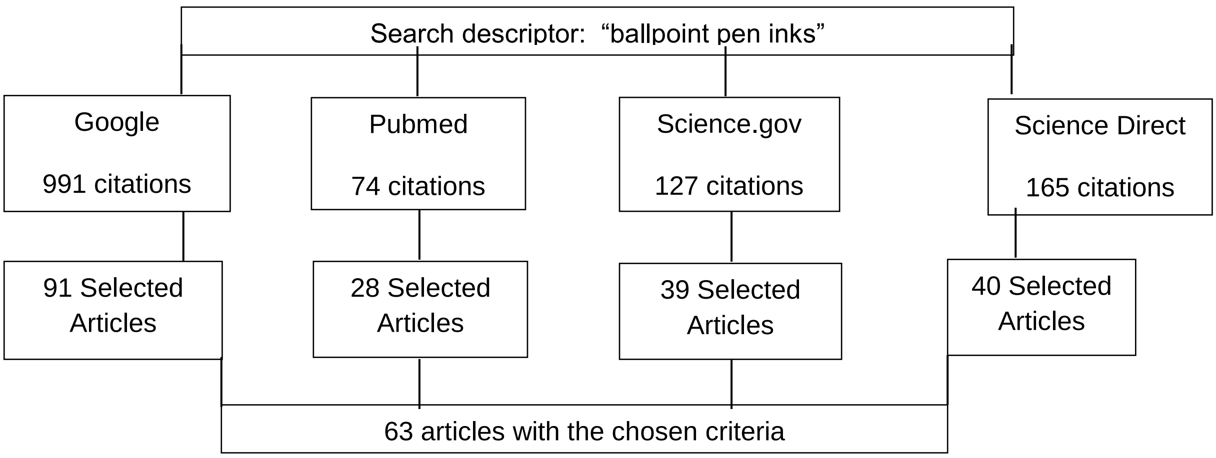

Figure 1. Strategy for the systematic review

3. Results

3.1. Ink characterization

Over the past few years, different methods have been developed for the ballpoint pen inks characterization regarding mainly the dyes and additives of the inks. Table 1 shows 49 recent published papers in this area[14-61], in chronologic order. For some methods, it is necessary to cut off a piece of the paper containing the ballpoint pen ink and proceed with an extraction, and the most used solvent is methanol. Those are destructive methods and there were required for the following techniques:

HPTLC (High Performance Thin Layer Chromatography)[14,16,27,29,31,43,44,47,50,58,59,61], Capillary Electrophoresis[33,57], ESI-MS (Electrospray Ionization Mass Spectrometry) [18,55], LDI-MS (Laser Desorption/Ionization Mass Spectrometry)[53], UV-Vis (UV-Vis Spectroscopy)[17,31,40-42,48,50,58,61] and Orbitrap Mass Analyzer[15,20]. The non-destructive methods, when the ink is analyzed directly from the paper, include the Luminescence Spectrometry[60], ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry)[54,56], FTIR (Fourier Transformed Infrared Spectroscopy)[16,21,25,28,37,38,41,45,46,48,50,51,52], Raman Spectroscopy[21-23,34,38,48], X-ray fluorescence[41,42], LIBS (Laser Induced Breakdown Spectroscopy)[26,39,49], Video Spectral Comparator VSC®6000[35,36], PS-MS (Paper Spray Mass Spectroscopy)[30], DSA (Direct Sample Analysis)[24], MAT 253 isotope ratio mass spectrometer[32] and digital images obtained from an iPhone[19]. Some of those techniques used the ink directly from the pen for the analysis.

Mass Spectroscopy (MS) and Spectroscopic methods are the main approaches for ink analysis. In MS, chemical species are ionized and separated according to their mass-to-charge ratio (m/z). Different ionization sources can determine the MS's versatility, adapted for different samples' use. Spectroscopic methods use electromagnetic radiation to transform the molecule from a ground-state energy level to an excited-state one[62]. Both spectroscopy and mass spectrometry chemical data can be visualized as a pattern in the multivariate space. Samples with similar pattern group together and those with distinct pattern will be separated in the multivariate space. By knowing this concept, the multivariate statistics or chemometrics (a mathematical tool used to maximize information that can be extracted from a data set) is an important tool which was widely used for the ballpoint pen inks differentiation and characterization. For the pen inks discrimination two statistical analysis were reported in the literature: the Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA)[63]. PCA consists in a data matrix transformation, in order to represent the largest variations of the data through a small number of factors. HCA is a useful analysis to determine the object resemblance and to identify similar and non-similar samples[63].

Table 1. Published studies on ink characterization. [i]HPTLC: High Performance Thin Layer Chromatography; [ii]GC-MS: G Chromatography/Mass Spectrometry; [iii]ATR-FTIR: Attenuated Total Reflectance Fourier Transformed Infrared Spectroscopy; [iv]UV-Vis-NIR: Diffuse Reflectance UV–Vis NIR Spectroscopy; [v]LC–DAD–ESI–MS system: Liquid Chromatography Coupled to Diode Array Detection and Electrospray Ionization Mass Spectrometry; [vi]LC-DAD-Orbitrap MS: Liquid Chromatography Diode Array Detection-Orbitrap Mass Spectrometry; [vii]LC-MS: Liquid Chromatography Mass Spectrometry; [viii]LIBS: Laser Induced Breakdown Spectroscopy; [ix]UPLC: Ultra-Performance Liquid Chromatography; [x]HPLC: High Performance Liquid Chromatography; [xi]PS-MS: Paper Spray Mass Spectroscopy; [xii]UV-Vis: Ultraviolet–visible spectroscopy; [xiii]VSC®6000: Video Spectral Comparator VSC®6000; [xiv]PLS-DA: Partial least squares-discriminant analysis; [xv]TLC: Thin-layer Chromatography; [xvi]LA-ICP-MS: Laser Ablation Inductively Coupled Plasma Mass Spectrometry; [xvii]LDI: Laser Desorption Ionization Mass Spectrometry; [xviii]ToF-SIMS: Time-of-Flight Secondary Ion Mass Spectrometry; [xix]ESI–MS: Electrospray Ionization Mass Spectrometry [xx]NACE: Non-aqueous Capillary Electrophoresis.

Samples (Available data in each study)	Sample Preparation	Method	Main Conclusions	Reference
78 ballpoint pens (40 red and 38 black pen inks)	Extraction from the paper with methanol	HPTLC[i] and GC-MS[ii]	"All the samples were completely differentiated using HPTLC. GC-MS discriminated red and black ballpoint pen inks with discrimination potential of 32.85% and 63.58%, respectively"	Saini and Rathore, 2018[14]
33 blue and 36 black ballpoint pens of different brands	Extraction from the paper with methanol	Q-Exactive[ii] Orbitrap Mass Analyzer / Chemometrics	"The analysis of ballpoint pen samples in a Q-Exactive® Orbitrap mass analyzer in positive and negative mode was able to differentiate the samples, even for inks of very similar color, and the method proved to be very sensitive"	Carvalho *et al*., 2018[15]
57 blue ballpoint pens of different brands and/or models	Direct analysis of the ink line on paper	FTIR[iii] and HPTLC[i]	"Pen ink samples were characterized by ATR–FTIR spectroscopy and discriminated on the basis of HPTLC and ATR–FTIR spectroscopy coupled with multivariate analysis. The approach of ATR–FTIR has proven out to be an effective tool for characterization of complex ink formulation"	Kumar & Sharma, 2017[16]
57 blue ballpoint pens of different brands and/or models	Direct analysis of the ink line on paper	UV–Vis-NIR[iv]/ Chemometrics	"It is concluded through this study that all the 57 blue ballpoint pen ink samples were differentiated on the basis of combined approach of diffuse reflectance UV–Vis-NIR spectroscopy and chemometrics"	Kumar & Sharma, 2017[17]
21 ballpoint pen inks (18 blue, 1 red, 1 black, and 1 green)	Extraction from the paper with methanol	LC–DAD–ESI–MS system[v]/ UV Detection	"As a result, a novel approach for the identification of dyes in the ballpoint pen inks by flow injection analysis with LC–ESI–MS and UV detection without using standard dye samples has been established. It can be an effective alternative to the existing LC–DAD–MS and IR spectroscopy methods"	Akhmerova *et al*., 2017[18]

20 blue ballpoint pens and 22 other types of pens	Digital images of the ink lines on paper	Digital images obtained from an iPhone and Chemometrics	"The proposed method was tested for discrimination between 42 blue pen inks of different types and brands and validated by independent validation (or test) samples"	Valderrama & Valderrama, 2016[19]
10 blue roller ball pens and 20 blue ballpoint pens	Direct analysis from small cuts of the ink line on paper	LC-DAD-Orbitrap MS[vi]	"The results showed that the established method is capable of detecting and identifying potential dyes in blue writing inks"	Sun *et al*., 2016[20]
11 black ballpoint pens from 11 different places	Direct analysis of the ink line on paper	FTIR[iii] / Raman Spectroscopy / Chemometrics	"This article has presented the potential combination of RS and FTIR with the statistical technique of PPMC and chemometric techniques of PCA, which can offer a powerful approach for source determination of unbranded ballpoint pen inks, compared with conventional direct visual examinations of the Raman and FTIR spectra alone"	Asri *et al.*, 2016[21]
30 ballpoint pens – 3 blue, 3 red (of 5 brands each)	Direct analysis of the ink line on paper.	Raman Spectroscopy / Chemometrics	"The results of this study demonstrate that PCA can be used to objectively interrogate ballpoint-pen inks of similar colour and, more importantly, of different brands"	Asri *et al*., 2016[22]
14 blue ballpoint pens of different brands and/or models	Direct analysis of the ink line on paper.	Raman Spectroscopy / Chemometrics	"The combination of Raman spectroscopy and chemometrics has proven to be useful to differentiate among different kinds of pen inks in complex multiclass problems"	Borba *et al*., 2015[23]
20 black and 20 blue ballpoint pens of different brands and/or models,40 non-ballpoint pens	Direct analysis from small cuts of the ink line on paper	Direct sample analysis (DSA)/ GC-MS[ii]/ LC-MS[vii]	"Of the three techniques utilized, DSA provided the greatest number of ink compound identifications and in more samples. However, no single method detected all the components of the ink formulations. For profiling purposes, it is therefore necessary to utilize more than one method, such as the combination of DSA, LC-MS, and GC–MS presented in this study"	Nguyen & Moini, 2015[24]
15 blue and 15 red ballpoint pens of 5 different brands and/or models	Analysis from small cuts of the ink line on paper	FTIR[iii] / Chemometrics	"Ballpoint pen inks of two different colours i.e. blue and red of five different brands were successfully resolved and differentiated after undergoing chemometric treatments of PCA"	Asri *et al*., 2015[25]
105 black and blue ballpoint pens from 12 different brands	Direct analysis from small cuts of the ink line on paper	LIBS[viii]	"The LIBS method provided comparable discrimination powers for the selected sample sets when compared to those obtained using LA-ICP-MS (discrimination from 99.8 and 100% of the sample pairs, depending on the sample subset under examination). LIBS is a suitable technique for the determination of elemental composition as part of a protocol for the examination of questioned documents"	Lennard *et al*., 2015[26]
12 black ballpoint pens of 4 different brands	Extraction from the paper with acetonitrile.	UPLC[ix] / Chemometrics	"The approach proposed here has successfully differentiated all pen pair thus achieving 100% discrimination power"	Lee *et al*., 2015[27]

11 black ballpoint pens from different places	Direct analysis of the ink line on paper	FTIR[iii] / Chemometrics	“The score plot of the PCA reveals seven clusters (five homogenous and two heterogeneous clusters) while the dendrogram of the HCA reveals six clusters (two homogenous and four heterogeneous clusters) which indicate that the unbranded black ballpoint pen inks may share similar ink formulations which can complicate their identifications”	Kamil *et al*., 2015[28]
9 blue ballpoint inks and 3 blue pen inks of different brands	A portion of pen and inks were dissolved in ethanol	HPLC[x]	“The developed method proved to be a powerful, low cost, and simple tool that allowed discriminating between different inks”	Hosu *et al*., 2015[29]
12 blue ballpoint pens of different brands	Direct analysis of the ink line on paper	PS-MS[xi]	“The results of these tests revealed distinct degradation behaviors which were reflected on the typical chemical profiles of the studied inks, attesting that PS-MS may be also useful to verify the fading of dyes thus allowing the discrimination of entries on a document. As proof of concept experiments, PS-MS was successfully utilized for the analysis of archived documents and characterization of overlapped ink lines made on simulated forged documents”	Ferreira *et al*., 2015[30]
48 blue ballpoint pens of 12 different brands	Extraction from the paper with methanol.	UV-Vis[xii] / UPLC[ix]	“UV-Vis spectral data were mainly produced by the colorant components (i.e., dyes) found in inks and UPLC may detect ink components other than dyes, i.e., additives. The Discrimination Power for UV-Vis and UPLC were determined to be 72.12% and 98.48%, respectively”	Lee *et al*., 2015[31]
27 ballpoint ink pens and 19 gel ink pens of different brands and colors	Ink taken directly from the pen	MAT 253 isotope ratio mass spectrometer	“The capacity of stable isotope ratios to differentiate among ballpoint inks as well as gel inks shows that stable isotope analysis may be a useful and quantifiable investigative technique for questioned document examination, although current sample size requirements limit its utility”	Chesson *et al*., 2015[32]
34 different classes of blue pens	Extraction from the paper with methanol	Capillary electrophoresis	“A 100% of discrimination was achieved between pen technologies, brands, and models, although non-reproducible zones in the electropherograms were found for blue gel pen samples. The two different batches of blue oil-based pens were also differentiated”	Calcerrada *et al*., 2015[33]
14 blue ballpoint pens of different brands and/or models	Direct analysis of the ink line on paper	Raman Spectroscopy / Chemometrics	“The combination of Raman spectroscopy and chemometrics has proven to be useful to differentiate among different kinds of pen inks in complex multiclass problems”	Borba *et al*., 2015[34]
25 different classes of blue pens	Direct analysis of the ink line on paper	VSC®6000[xiii]/ PLS-DA[xiv]	“The method showed to be robust in relation to different paper types and batches of pens. The analysis of a blind test indicates that the method is also free of biased judgments of the analyst and robust regarding the handwriting of different individuals”	Silva *et al*., 2014[35]
55 different classes of black pens of 6 different brands and/or models	Direct analysis of the ink line on paper	VSC®6000[xiii]/ PLS-DA[xiv]	“The results showed that PLS-DA presented a high discrimination power when associated with the spectra obtained by the VSC®6000. The method enables the correct discrimination of black inks of different pen types, brands and pen models”	Silva *et al.*, 2014[36]

63 ballpoint pens (black and colored) of different brands and/or models	Direct analysis of the ink line (signatures) on paper	FTIR[xi]	"Micro-ATR FTIR was found to be feasible for differentiating ballpoint pen inks used for signatures in documents; differentiating the inks used for different signatures written with ballpoint pens will be useful for judging the authenticity of signatures in questioned documents. The origin of the ballpoint inks as well as the sequence of intersecting lines between signatures with two different ballpoint pen inks could be determined using micro-FTIR"	Nam *et al*., 2014[37]
71 blue ballpoint pens	Direct analysis of the ink line on paper	FTIR[iii] / Raman Spectroscopy	"The result indicated that Raman spectroscopy could easily remove the interference caused by the paper which could hardly be removed with infrared spectroscopy. No sample preparation was required and only 30s was needed for each sample in the optimized method. The method proved to be fast, accurate, non-destructive and could be easily applied to the real cases. The primary survey on inks from different market indicated five kinds of inks could be identified"	Liu *et al*., 2014[38]
34 blue, 30 black and 21 red pens (40 ballpoint pens, 29 gel pens, 6 porous point pens and 10 rollerball pens) of 17 brands	Direct analysis of the ink line on paper.	LIBS[viii]	It was determined that the LIBS method is capable of revealing qualitative elemental differences between ink samples. The discrimination power of this method was found to be 83, 82 and 61% for blue, black and red inks, respectively. Inks produced by the same producer were able to be differentiated in some cases"	Kula *et al*., 2014[39]
12 blue, 12 black and 12 red ballpoint pens of 2 different brands	Extraction from the paper with ethanol	UV-Vis[xii] / Chemometrics	"The results of this study demonstrates that conventional and low cost UV-Vis spectroscopy when coupled with chemometrics techniques can became a powerful tool that can be employed for forensic question document analysis"	Ismail *et al*., 2014[40]
7 ballpoint pens (4 blue and 3 black) of different brands	Ink line on paper and ink line on paper extracted with methanol	UV-Vis-NIR[iv]/ FTIR[iii]/ X-ray fluorescence spectroscopy/ TLC[xv]	"After the author knowledge, this is the first time when a comparative trichromatic analysis of some colored samples registered such as and for their extracts has been applied in order to assess the contributions of pigments and organic dyes used as chromophore agents. This original approach seems to be very efficient in discriminating various brands of ballpoint pen inks when it is sustained by complementary data provided by infrared spectroscopy, thin layer chromatography and elemental analysis performed by X-ray fluorescence spectroscopy"	Feraru *et al*., 2014[41]
6 ballpoint pens (3 red and 3 black) of different brands	Ink line on paper and ink line on paper extracted with methanol	X-ray fluorescence/ TLC[xv]/ UV-Vis-NIR[iv]	"Corroboration of trichromatic analysis, particularly that performed in methanolic extracts, with TLC data provides a valuable tool for discriminating of ballpoint inks within the same coloristic pallet and also for assessing some components by comparing with reference dyes available from adequate data bases"	Feraru *et al*., 2014[42]
12 black ballpoint pens of different brands	Extraction from the paper with methanol	HPTLC[i]	"The composition of black pen inks was found to be homogeneous and the proposed method showed good repeatability and reproducibility. The proposed HPTLC technique is useful for the precise discrimination of black ballpoint pen inks"	Lee *et al*., 2014[43]
12 blue ballpoint pens of different brands	Extraction from the paper with methanol.	HPTLC[i]	"The discrimination power (DP) of HPTLC technique to analyses blue ballpoint pen inks was determined to be around 89.40%"	Lee *et al*., 2014[44]

blue pens of 3 types: ballpoint (5 brands), roller ball (2 brands) and gel (3 brands)	Direct analysis of the ink line on paper	FTIR[iii] / Chemometrics	"Infrared Spectroscopy associated with linear discriminant analysis, using SPA, GA and SW algorithms for variable selection were successful employed to classify blue ink pens by type (gel, rollerball and ballpoint) and by brands"	Silva *et al*., 2013[45]
56 black ballpoint pens, of 14 different brands	Direct analysis of the ink line on paper	FTIR[iii]/ Pearson correlation	"Micro-ATR FTIR spectroscopy is reproducible and can potentially be used to differentiate pens of the same make, but different models"	Lee & Jemain, 2013[46]
13 black ballpoint pens of different brands	1 cm of each ink barrel and extraction with ethanol	HPLC[x]/ Chemometrics	"The results suggest that the HPLC profile of inks of different brands differ due to their similarities and differences in the chemical compositions. The results concurred with the PCA. Combination of HPLC and chemometric techniques provided a more objective interpretation of the results for the analysis of black ballpoint pen inks for forensic purposes"	Halim *et al*., 2013[47]
18 ballpoint pens (10 blue, 3 red, 3 black and 2 green)	Direct analysis of the ink line on paper	UV–Vis[xii] / FTIR[iii] / Raman Spectroscopy	"The methods used in this study such as reflected infrared, infrared luminescence, FT-IR spectroscopy, Raman spectroscopy, UV-Vis spectrometry and chromatic analyses in CIE-L*a*b* are efficient methods in document analyses, since these methods do not alter the documents"	Feraru *et al*., 2013[48]
21 blue ballpoint pens of 10 different places	Direct analysis of the ink line on paper	LA-ICP-MS[xvi]	"The LA-ICP-MS methodology has provided higher DPs than other conventional methods or techniques, such as visual comparison that lead to more subjective results or separation techniques which require tedious sample preparation"	Alamilla *et al*., 2013[49]
10 blue ballpoint pens of different brands	Ink line on paper and ink taken directly from the pen	UV–Vis[xii]/ FTIR[iii]/ HPTLC[i]	"The results proved that the UV–Vis spectra are effective and powerful tool to separate blue ballpoint pen ink in most cases rather than IR and TLC"	Senior *et al*., 2012[50]
155 black ballpoint pens of 9 different brands	Direct analysis of the ink line on paper	FTIR[iii]/ Chemometrics	"The results of the study have demonstrated the ability of micro-ATR-FTIR spectroscopy to produce an informative spectrum for classification, differentiation and identification of inks via multivariate analysis techniques"	Lee *et al.*, 2012[51]
24 black ballpoint pens, of 6 different brands	Direct analysis of the ink line on paper	FTIR[iii]/ Chemometrics	"All six different pen varieties could be grouped into three clusters according to their brands via DA. Discrimination power of the proposed methods was 86.67%"	Lee *et al.*, 2012[52]
33 blue ballpoint pens of different places	Extraction from the paper with ethanol	LDI-MS[xvii]	"This study has confirmed the high discrimination potential of LDI-MS combined to minimal preparation and analysis time"	Gallidabino *et al*., 2011[53]
24 blue ballpoint pens of 7 models and 5 different brands	Direct analysis of the ink line on paper	ToF-SIMS[xviii]	"Minimal sample preparation and analysis time, the simultaneous acquisition of organics and metals, and ability to analyze trace amounts gives this technique advantages over others currently utilized in the forensic field. It was indicated that pens from the same manufacturer, but discrete batches, can be significantly different"	Denman *et al.*, 2010[54]

18 black pens (6 ballpoints, 6 gels, and 6 rollerballs)	Extraction from the paper with methyl alcohol, ethyl alcohol or benzyl alcohol	ESI-MS[xix]	"The results of this study provide a reliable method of collecting writing ink samples with minimal destruction to the document, an efficient extraction method, and an ESI-MS detection method which can be used to distinguish between freshly deposited inks and to tentatively identify vehicles and dyes contained within the ink formulation"	Williams *et al.*, 2009[55]
13 blue ballpoint pens	Direct analysis of the ink line on paper	TOF-SIMS[xviii]	"TOF-SIMS can be used for the analysis of ballpoint pen inks producing mass spectra that were highly characteristic of the constituent dyes and inorganic substances used in their formulations. TOF-SIMS was also shown to be capable of analyzing ink containing a mixture of dyes, initially separated by thin-layer chromatography, directly on the chromatographic material"	Coumbaros *et al.*, 2009[56]
120 black ballpoint pens of different brands	Extraction from the paper with methanol	NACE[xx]	"The black ballpoint pens from the same group may be further distinguished by cluster analysis based on the content of different dyes and some unknown peaks"	Zou *et al.*, 2008[57]
36 ballpoint pens (6 blue, 6 red and 6 black) of 2 different brands	Extraction from the paper with ethanol	UV–Vis[xii] / HPLC[x] / Chemometrics	"Ballpoint pen inks that were difficult to discriminate previously on the basis of their UV-Vis spectra alone, were successfully discriminated and resolved after undergoing chemometrics treatments"	Dzulkiflee *et al.*, 2008[58]
41 blue ballpoint pens of different brands	Extraction from the paper with methanol	HPLC[x] Image analysis	"This new method allowed discriminating among different pen inks with a high reliability and the discriminating power of 92.8%"	Djosan *et al.*, 2008[59]
10 black ballpoint pens of different brands	Direct analysis of the ink line on paper	Luminescence Spectrometry/ Chemometrics	"The application to inks was evaluated on a pair-wise basis, through examination of both calibrated and handwritten ink-lines. In the former case, excellent discrimination was obtained with a discriminating power across this set of pens of 78% at the 99% confidence level and 87% at 95% confidence. For written samples, discrimination was less good, though still better than filtered light, with discriminating powers of 60% and 64% respectively. This difference is attributed to poorer spectral quality and increased sample inhomogeneity when dealing with ink-line writing"	Adam, 2008[60]
25 black ballpoint pens of different brands	Ink line on paper extracted with ethanol	UV–Vis[xii] / HPLC[x] / Chemometrics	"For the UV-vis spectroscopy data, the interpretation of the loadings for the first few principal components showed that both the pen inks and the extracted ink lines may be classified in an objective manner and in agreement with the results of parallel thin layer chromatography studies"	Adam *et al.*, 2008[61]

3.2. Ink dating

Despite the static dating method, which is related to ink characterization, there are two possibilities for ink dating, considering the inks' components transformations with time[3,4]:

(a) Relative dating methods, when there is a suspicion that the document was partially forged at a different date. In this case, the document must contain two questionable inks and the inks' components concentration are measured and compared.

(b) Dynamic dating method, based on the ink's components concentration measurement, considering the ink transformations over time (like the remaining solvent quantity or the detection of dyes' degradation).

For both relative and dynamic dating methods, it is necessary to have methods that are capable to detect the ink changes over time. Table 2 shows the most recent studies involving those methods[64-78]. The majority of the studies are based on the monitoring of solvents as they evaporate over time, but there are also studies based on the degradation of the dyes or resins.

Several studies have been using the 2-PE solvent quantification according to the inks' age, and gas chromatography coupled to mass spectrometry (GC–MS) or coupled with Flame Ionization Detection (GC-FID) is still the established method for the 2-PE quantification[64,65,67,71-73,78].

As for the dyes degradation with time, the following methods have been recently evaluated in the literature: UV-Vis Spectrophotometry[66,68,76]; HPLC-DAD (High Performance Thin Layer Chromatography Diode Array Detection)[67]; Paper Spray Mass Spectrometry[69]; DART-MS (Direct Analyses in Real Time Mass Spectrometry)[74]; EASI-MS (Easy Ambient Sonic-spray Ionization Mass Spectroscopy)[75]; LDI-MS (Laser Desorption Ionization Mass Spectroscopy)[76] and Capillary Zone Electrophoresis/Micellar Electrokinetic Chromatography/MALDI-TOF-MS (Matrix-assisted Laser Desorption/Ionization Time-of-Flight Secondary Ion Mass Spectrometry)[77].

Table 2. Studies on ink dating by separation and spectrometric techniques. [i]GC-MS: Gas Chromatography/Mass Spectrometry; [ii]UV-Vis-NIR: Diffuse Reflectance UV–Vis NIR Spectroscopy; [iii]HPLC-DAD: High Performance Liquid Chromatography with Diode Array Detection; [iv]UV-Vis: Ultraviolet–visible spectroscopy; [v]PS-MS: Paper Spray Mass Spectroscopy; [vi]GC-FID: Gas Chromatography Flame Ionization Detection; [vii]DART-MS: Direct Analyses in Real Time Mass Spectrometry.

Main Compound for Ink Dating and Samples	**Sample preparation**	**Technique / detector**	**Main Conclusions**	**Reference**
Standard 2-phenoxyethanol (solvent)	Ink line cut from paper extracted with methanol.	GC–MS[i]	"This study performed the figures of merit evaluation of the quantification of 2-PE using GC/MS, testing the main parameters involved in the reliability of the method (linearity, repeatability, limits of detection and quantification, accuracy and robustness). After, based on a full factorial design with four factors and two repetitions, the authors tested kind of paper, grammage of paper, ink color and three ink ages, to verify the paper influence on the quantity of 2-PE from ink, trough GC/MS analysis"	Carvalho *et al*., 2018[64]
2-phenoxyethanol (solvent) - 25 different inks chosen as representative of the different ageing behaviours	Ink line cut from paper extracted with chloroform	GC–MS[i]	The results showed that all ageing parameters were significantly influenced by the ink composition and a wide range of values were obtained for each parameter over the studied time range. The ageing parameters using PE and artificial ageing in their calculation (PE quantity, R%, R%* and RNORM) presented a descending trend over the whole time range, demonstrating their potential to date a document created a few weeks to a few months before the analyses. The PE quantity and RNORM ageing curves distributions were highly correlated and influenced by inks containing a high concentration of PE. Thus, these two parameters would mainly work to date younger inks up to a few weeks. From the two, RNORM showed the strongest differences between young and old samples and is thus more promising to estimate the age of ink entries of unknown origin"	Koenig *et al.,* 2018[65]
Total ink - 48 samples of a commercial ink (Inoxcrom®)	Extract of the ink from the cartridge and then spread on white paper using a different brush for each ink	UV–vis-NIR[ii] / Chemometrics	"UV–vis-NIR spectrometry combined with Partial Least-Squares (PLS) method for ink dating reported in this paper named DATUVINK demonstrates that diffuse reflectance UV–vis-NIR spectroscopy combined with chemometrics is a powerful tool for predicting the age of inks deposited on paper. In addition, it is worth noting the advantage of this methodology in this type of analysis since it would be rapid and non-invasive, needing little to no sample treatment"	Ortiz-Herrero *et al*., 2018[66]
Solvents and dyes - 8 samples from a blue ballpoint pen and 8 samples from	Ink line cut from paper extracted with methanol	GC–MS[i] / HPLC-DAD[iii]	"The combined GC–MS and HPLC-DAD method that we propose allows the quantification, with a single extraction of ink on paper, of 17 solvents and 13 dyes typically used in modern ballpoint pen inks. The possibility to measure both solvents and dyes from a	Diaz-Santana *et al*., 2017[67]

a black ballpoint pen			single sample using a combined method enables the concentrations obtained to be normalized, eliminating the effect of variations in sample mass between sample extractions, a factor that results from variations in the thickness or pressure of application of pen strokes”	
Total Ink – Samples from a blue ballpoint pen	Ink line cut from paper extracted with methanol	UV–Vis[iv] / Chemometrics	“In the proposed study, UV–Vis spectroscopy along with the multiple linear regression analysis is used for predict the dating of ink”	Sharma *et al*., 2017[68]
Total ink - 6 black ballpoint pens	Ink lines cut from the paper without any sample preparation	PS-MS[v]	“The feasibility of the method on forensic investigations was also demonstrated in three different applications: (1) analysis of overlapped fresh ink lines, (2) analysis of old inks from archived documents, and (3) detection of alterations (simulated forgeries) performed on archived documents”	Amador *et al.,* 2017[69]
Total ink - Luminescent ink components from blue and black ballpoint pens and ink pads	Intersecting lines of different inks and one ink without any intersection were applied on different paper qualities	Pictures were taken with the aid of a video comparator apparatus	“We could show that some inks contain luminescent components that migrate/diffuse into the paper material, preferably detectable in the area of an intersected primary ink line. This propagation continues for several months, probably even years. Migration speed curves give logarithmic functions. An individual ink ageing curve can be drawn for any questioned document, as soon as there is a luminescent zone beside the visible ink line”	Hofer and Bako, 2016[70]
2-phenoxyethanol (solvent) - 3 different inks labelled 1688, 1774 and 1892, supplied in pen cartridges	Ink line on paper extracted with chloroform	GC–MS[i]	**“**This work confirmed that ink dating methods using liquid extraction followed by GC/MS analysis were easily applicable in a laboratory, proved to be sensitive enough for dating purpose and allowed measuring a wide range of concentrations corresponding to the concentrations commonly found in ink strokes. Four different ageing parameters were evaluated: the quantity of PE, the relative peak area (RPA) between different solvents and two solvent loss ratios calculated respectively from the PE quantity (R%) and the RPA values (R%*). Among those, two particularly interesting parameters, RPA and R%* values for slow, medium, and fast drying inks were reported for the first time in the literature. In terms of variability, R% proved to be the most repeatable parameter as the maximal RSD obtained was 16%. In opposition, the R% showed the highest variability with RSD values going up to 38% for older samples. Thus, when RPA can be calculated, the R% should always be preferred to the R% in order to reduce significantly the variability for the analysis of older ink samples”	Koenig *et al.,* 2015[71]
Solvents – 2 blue and 2 black ballpoint pens	Multiple solid-phase microextraction (MHS-SPME)	GC–MS[i]	“The results of this investigation showed that the volatile components of ballpoint pen inks can be easily monitored by HS-SPME technique”	San Roman *et al*., 2015[72]

2-phenoxyethanol (solvent) – 8 blue and 8 black ballpoint pens	Ink line on paper extracted with methanol	GC–FID[vi]	The analyzed pens did present differences in the initial quantity of 2-phenoxyethanol. Black pens had more homogeneous quantities than blue pens, which had higher variability	Carvalho, 2014[73]
Total ink - 1 black ballpoint pen and other types of pens	The analysis was performed directly from the ink line on paper	DART-MS[vii]	“During the first few months after an ink is written on paper, its DART spectrum changes as the more volatile components of the ink are lost, but the changes have generally attenuated before a year has passed”	Jones & McClelland, 2013[74]
Dyes – blue and red ballpoint pens/real aged documents	Ink lines directly from the paper surface without any sample preparation	EASI-MS[viii]	**“**Using EASI-MS performed directly on paper surfaces, we have been able to collect fingerprint spectra with characteristic dye profiles for different inks. A linear correlation for accelerated aging and degradation products for some of the most typical ink dyes has been obtained, demonstrating that this cascade of products works as a reliable ‘chemical clock’ for ink aging, particularly when relative ages are compared”	Lalli *et al*., 2010[75]
Crystal Violet (dye) – 3 blue ballpoint pens	Compare the degradation pathways of the pure dye in water and ethanol upon exposure to xenon light	UV-Vis[iv] / LDI**[ix]**	**“**Significant differences have been observed in the products and the kinetics of the degradation. N-demethylation, an expected decomposition process, was found to take place only in aqueous solution and kinetics calculations showed that the degradation occurred 2.5 times faster in ethanol compared to water. The degradation of crystal violet in inks from four ballpoint pens on paper was also studied for entries made over 2–3 years. It was observed that degradation reactions were quenched by the presence of another dye due to competitive absorption. It was also observed that the thickness of a stroke (concentration of ink) influenced the degradation process. In the absence of light only one ballpoint pen showed slight degradation”	Weyermann *et al*., 2009[76]
Standard blue ballpoint pen dyes	Commercial Crystal Violet analyzed before and after light exposure	Capillary Zone Electrophoresis / MALDI-TOF-MS[x]	**“**This study successfully evaluated different methods of pen ink analysis, CE (under CZE and MEKC modes) and MALDI-TOFMS. Various N-demethylation products of CV were separated using CZE and identified by means of MALDI-TOFMS. These methods are useful in dating inks”	Shih *et al*., 2008[77]
2-phenoxyethanol (solvent) – 15 different blue and black ballpoint pens	Ink line extracted from the paper, heated at 200ºC	Thermal Desorption / GC-MS[i]	**“**The results demonstrate that heating ballpoint ink on paper influences the chemical composition, suggesting a reason for the observed age-dependent behavior. The application range of the proposed procedure was studied by analyzing 85 different types of ballpoint pen inks over a period of 1.5 years”	Bugler *et al*., 2008[78]

4. Discussion

Ballpoint pen inks' characterization and dating are frequently requested analysis in judicial cases, and most commonly for blue and black ballpoint pens. There is no standard formula for the ballpoint pens manufacturing, so the components' quantities and even solvents, dyes and resins may vary between different brands of pens, and this may vary between different regions too[4,78]. In that context, it is very important to have methods to differentiate the ballpoint pens from each other. Sometimes the fact of proving that two different pens were used in the same document may even lead to some answers in a specific case; for example, the adulteration of a document's writing part through the erasure and re-writing with a ballpoint pen of similar color[79]. It is also possible to proceed with indirect dating using the chemical analysis of an ink followed by comparison with known samples in a reference collection; some ink formulas may be discontinued or known to be characteristics of a particular sale's period – this is the static dating method[3,80].

This manuscript discusses technological advances and novel methods that have shown potential to improve discrimination and characterization of ink profiles. Every one of those listed articles in Table 1 reported good characterization and differentiation between ballpoints originating from different sources, indicating there are several possibilities of methods to analyze and differentiate ballpoint pen inks. Those methods can provide answers when it is necessary to determine if an ink was written in a document at a later date (backdating) or to determine date authenticity. For Forensic application, non-destructive methods are much better techniques, because the analysis is performed directly in the document without the need to cut or consume a part of it, which guarantees the possibility of counterproof. Also, since all methods has shown good results, it is not necessary for Laboratories to have the most expensive equipment to perform ballpoint pen inks analysis.

Fewer articles have addressed both, the methods' ability to distinguish different ink formulas and to associate those from the same formulations. A thorough evaluation of the method's application and validity should address false positive and false negative error rates. Moreover, most of the studies have a limited number of specimens or manufacturing information not fully traceable. Therefore, these findings should be considered as proof of principle, but larger ink collections would be necessary to expand their full assessment for ink dating.

Regarding the dynamic dating methods, which evaluate the ink's transformations with time, GC-MS is the prevalent method used for the quantification of 2-PE solvent loss over time using traditional sampling or SPME (*Solid-phase Microextraction***)**. The most recently published article, Koenig and Weyermann (2018)[65] analyzed 25 different ballpoint pen inks, to quantify the 2-PE through GC-MS method. They evaluated 7 different aging parameters, in order to establish an interpretation model to its ink dating' legal use. Nevertheless, there are still more studies to be done, to proper evaluate all the variation that influences the 2-PE evaporation over time and how to use that as a standard protocol. First of all, once on paper, 90% of the ballpoint pen ink solvents' evaporate in a few minutes, but the rest of it continues to evaporate and can take up to only two years[4]. As the ballpoint pens' formulas vary among different pen brands, different initial quantities of ink's components might influence in the analysis conclusion. It is also known that different writing fists have different pen pressures on the support paper, releasing more or less ink quantity, so it could also change the ink's age analysis results. For destructive techniques such as GC-MS, it is necessary to extract the same amount of samples, standard and questioned, because the analysis is based on inks components' quantities. Another aspect to consider is the document's paper type and its influence on the ink's component extraction[2,71,72].

Approaches that evaluate the dyes' degradation have gained attention through different techniques. Although good results have been shown, there are still some precautions to be aware of. For instance, dyes degrade in contact with light and high temperatures, so the document's storage conditions are critical for the ink's age behavior. Aginsky (1998)[81] has compared two ink-dating methods: the first one analyzing the solvents' evaporation and the second one using the dyes' degradation, and both methods were measured with a substance extraction coefficient, as a function of inks' age. In order to extract the volatile ink components, which are fully immersed on resins, it is necessary the complete resins dissolution and they are resistant to it. The resins extractions do not vary between ink from the pen cartridge and ink from the paper, so the observed variation between old and recent pen strokes is related to the remaining solvent quantity extracted from old ink strokes' resins, correlating with the age. To extract dyes, although, it is known that the dyes composition is the same inside and outside the pen cartridge. Dyes are not bonded to resins and are easily extracted. The extraction percent obtained by Aginsky shows that the dyes extraction coefficient are always higher than the real value because its extraction is easy, unlike the solvent's extraction, and this does not correlates with the ink age. Consequently, the dyes extraction is vulnerable to unknown factors. Andrasko and Kunicki (2005)[82] also studied the differences about the ink composition, and concluded that there were no changes between dyes from the pen cartridge and dyes from a pen stroke on paper with 6 years old. Additionally, they concluded that different brands of pens have different Crystal Violet, Methyl Violet and Tetramethyl Pararosaniline quantities. Some pens presented 6% of Tetramethyl Pararosaniline, commonly used as a degradation marker, while other pens presented 15% of this substance, even though those pens had the same age. In this same paper, authors analyzed one pen from 1997 to 2004 and found no differences in Tetramethyl Pararosaniline proportion, so there was no degradation of this dye in seven years.

Lastly, another aspect to consider in ink dating is the possibility of artificial aging, which have a large number of factors that might be used to make a document looks older than it is, like the excessive light exposure and the high temperature storage[83].

5. Conclusion

This systematic review presented different method approaches for ink-dating analysis. However, currently, only a few answers may be given regarding ink's age, and most of the performed exams are relative dating methods, when it is possible to evaluate two inks and compare their ages. The methods' improvement and interpretation, with research, might provide a possible working protocol in the future for Forensic Document Laboratories and its legal use. It is also essential to provide forensic experts with proper training for the analytical methods, data analysis, quality control, and interpretation of the evidence.

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