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REVIEW ARTICLE

Analysis of Ballpoint Pen Inks by Chromatographic and Spectroscopic Techniques

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Key words: Ink analysis, Spectroscopy, Chromatography

Abstract

The current review focuses on ballpoint pen analysis and the many methods and procedures used to determine ballpoint pen analysis. Ballpoint pens are analysed using both destructive and non-destructive techniques. Paper chromatography, Thin layer chromatography, High-pressure liquid chromatography, Raman spectroscopy, Infrared, UV light examination, and electrophoretic techniques like capillary electrophoresis are some destructive and non-destructive techniques mentioned in the article. The article examines the inks used in ballpoint pens from 1954 to 2019. Both combinations of chromatographic and spectroscopic techniques provided more reliable results.

Introduction

Questioned papers (QD) are those that are suspected of being false or have a questionable source, history, or legitimacy. Because questioned documents are frequently linked to criminal activities such as fraud, forgery, blackmail, illicit drug trafficking, and homicide, thorough and systematic examinations of them may aid in the resolution of crimes involving the documents (Arsi *et al.*, 2015). Documents are a necessary component of our daily lives (Menżyk *et al.*, 2016). Because it is linked to human daily life, documents are an inevitable evidencein forensic investigations. Ink analysis is a crucial method that might provide essential details about the paper in issue. When written with writing instruments such as a pencil, ball-point pen, fountain pen, gel pen, or other substances that can be used for the same purpose, the majority of them are made of paper and finished in ink Discrimination of inks and/or identification of their source are crucial issues when examining documents for forensic reasons . The classification and comparison of chemically complicated mixes of dyes, pigments, and other elements, which are generally present in handwriting on a document, is the focus of forensic ink examination (Feraru & Meghea, 2014). The forensic examination of inks is principally concerned with the classification and comparison of chemically complex mixtures of dyes, pigments and other materials, usually present as writing on a document. Over recent years, technological developments have rapidly expanded the range of pen designs and ink compositions used throughout the world (Adam *et al.*, 2008). Colorants, a vehicle, and additives make up the majority of inks used in writing tools. Colorants account for around 20% (m/m) of the total and are classified into dyes and pigments. Carriers or vehicles account for around half of the total (m/m) and are typically organic solvents or water. Additives have a wide range of properties due to their nature (resins, viscosity adjusters, antioxidants, surfactants, softeners, corrosion inhibitors, lubricants, even tags as rare earth chelates (Alamilla *et al.*, 2013).

Ballpoint pens

John Loud, a leather tanner, devised a roller ball tip marking pen with its own ink reservoir in 1888, which gave birth to the ballpoint pen. Loud's idea was refined in terms of design and ink formulation fifty years later, and Ladislas and George Biro eventually commercialised it. A complex blend of colours, pigments, solvents, resins, viscosity adjustors, and ball lubricants make up ballpoint pen ink (Colwell & Karger, 1977). Ball-point pen use has expanded dramatically over the last decade as a result of advancements in a formulation that have resulted in a permanence comparable to that of fountain pen inks. Ball-point inks are widely used while examining questioned papers due to their rising use (Nunkoo *et al.*, 2016). Inks for ballpoint pens are viscous liquids comprising a mixture of colours and pigments, organic solvents, and additives such as antioxidants, resins, preservatives, softeners, and trace elements (Brown & Kirk, 1954). The case of the pen is constructed of plastic the ink reservoir, as well as a ball that is The ink was continually coated on the surface. When you're in the act of As you write, the ball revolves and eventually comes to a halt. the ink is transferred to the writing substrate (Asri *et al.*, 201). The

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Colourant	Ink component	Characteristics	Functions
	Dyes Pigments	Organic compounds , soluble in vehicle Organic / inorganic compounds, Provide desired apperance	insoluble in vehicle (colour)
Vehicle	Solvents Resins	Organic solvents , water , and their mixtures Marcomolecular organic compounds of both natural and synthetic origin	Dissolve the colourant in the dye and deliver it to substrate Suspend , deliver and bond pigments to substrate ; provide desired viscosity
Additives	Surfactants Biocides Waxes	Soaps or detergents Compounds of natural or synthetic origin Hydrocarbon waxes , greases , vaseline	Decrease the surface tension of ink. Inibits microbial development Regulate ink flexibility

actual composition of pen inks is a trade secret and unique to each brand and manufacturer. The fundamental goal of ink analysis is to see if two bits of written text came from the same ink. To identify between different inks used in ballpoint pens, several analytical and spectroscopic techniques have been applied, and they are usually grouped into two major categories: destructive/semi-destructive and non-destructive/non-invasive (Brown & Kirk, 1954).

Chromatography

Chromatography is a separation process for sample components. A stationary phase and a mobile phase are used to separate the components. This separation occurs as a result of the substance's molecules' affinity for the stationary phase. Chromatographic techniques, which aid in the detection of questioned papers, have enabled the comparison and inspection of ink (Ferreira *et al*., 2015).

Spectroscopy

A beam of electromagnetic rays of a specific wavelength is sent through the substance in spectroscopy. Some of the energy beams are absorbed by the substance. The leftover radiations strike a photoelectric cell, causing variations in the circuit's current. On graph paper, the modifications are recorded. The unknown material can be identified by comparing the graphs to those of the known materials. In a nutshell, it's the study of how electromagnetic radiation interacts with a material. The material's electrons are scattered, emitted, or absorbed as a result of this.

Records of chromatographic and spectroscopic analysis of ballpoint pen inks (1954 to 2019)

Ref.- Brown & Kirk (1954). TI- Blue , Black , Red , Green. MS- Horiżontal paper chromatography. Aim-Differitation of blue ballpoint pen inks. F-Identification of every ink individually was not found possible from the dye components separated by chromatography. Identification of nearly all of the inks was possible from the chromatogram combined with a study of the ink line to reveal major differences in a vehicle.

Ref.- Crown et al. (1961): TI-Ball point pen (Blue) Md - Identification by Dye composition. Aim- Differiatation of Blue ballpoint pen inks. Findings- Depending on the dyes present, blue ballpoint inks can be split into numerous distinct types.

Ref.- Lyter (1982) TI- Ballpoint pen. Md- High-pressure liquid chromatography (HPLC) Aim- Examination of ballpoint pen ink. Findings- The HPLC system allowed the detection of quantitative and qualitative differences among the ten ink formulations examined.

Ref.- Roux *et al.* (1999): TI- blue,black. Md- FLE (Filtered light examination, M SP (Mass spectroscopy), T LC (Thin layer chromatography). Aim- To study evidential value of Black ballpoint pens in Austrilla. Finding- The Discriminating powers of individual and combined techniques. FLE of black is 0.83, MSP is 0.83, TLC is 0.98, combined sequence is 0.99 For blue FLE IS 0.96, MSP is 0.83, TLC is 0.99 , combined sequence is 0.99

Ref.-Fabianska & Trżcinska (2001): TI- Blue, Black, Liquid inks Md-Optical examination (video spectral Comparator) Raman spectroscopy, TLC, Infrared spectroscopy Aim- Differitation of ball point pens & Liquid inks Finding-Raman spectroscopy method could serve as a supplement to the optical method.

Ref.- Weyermann et al. (2007) TI-Ball point pens Md - GC/MS (Gas chromatography, mass spectroscopy) Aim - Study of drying of ball point pen ink on paper Findings- 94% of the ballpoint pens were found to contain phenoxyethanol and 61% were found to contain phenoxyethoxyethanol. Benżyl alcohol (61%) and propylene glycol (54%) were also found in several ballpoint pen inks.

Ref.- Zieba-Palus & Kunicki (2006) TI-Ballpoint pens, gel pen inks. Md- Micro FTIR , Raman spectroscopy , X- ray flourescence spectroscopy Aim-Application of the micro- FTIR spectroscopy, Raman spectroscopy and XRF method examination of inks. Findings-90% of samples could be distinguished efficiently using these techniques on the basis of type and colour

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Ref.- Kher (2006): TI-Ball point pens. Md- HPLC & IR, Principal component analysis, linear discriminant analysis Aim- Forensic classification of ball point pen inksFinding- PCA separated 60.7% of the pen pairs and LDA provided a correct classification of 62.5% of the pens analyżed by IR. HPLC coupled with chemometrics provided better discrimination of ballpoint pen inks compared to IR.

Ref.-Causin *et al.* (2008) TI- Ball point pen (Black, Blue) Md- U.V spectroscopy, TLC, FTIR (fourier transform infrared spectroscopy) Aim- Discriminatio n potential & forensic analysis of black blue ball point inksFindings-The discrimination power for UV-VIS, TLC, and FT- IR was determined to be 100% and 98% for the black and blue inks, respectively.

Ref..-Geiman *et al.* (2009)TI-Ball point pens Md- Raman spectroscopy & surface enhanced raman scattering Aim-Analysis of synthetic dyes found in ball point pen inksFinding- High fluorescence background and poor spectral quality impair Raman spectra, yet SERS proved to be a superior approach. Data can also be collected directly from a TLC plate using SERS.

Ref.-Senior *et al.* (2012). TI-Ballpoint pen (Blue) M d - Principal component analysis of UV- Vis Absorption spectra, Infrared, HPTLC Aim-Characteriżation and Dating of blue ball point pen Finding- UV–Vis spectra are effective tool to separate blue ballpoint pen ink in most cases rather than IR and HPTLC.

Ref.- Lee et al. (2014)a TI- Ball point pens (Black) M d - HPTLC (High performance thin layer chromatography) Aim-Analysis of dyes in black ball point pen Finding- The proposed HPTLC technique is useful for the precise discrimination of black ballpoint pen inks.

Ref..- Lee *et al.* (2014)b TI- Ball point pens (Blue) M d - HPTLC Aim-Forensic analysis of blue ball point on question documents Finding-The discrimination power (DP) of HPTLC technique to analyses blue ballpoint pen inks was determined to be around 89.40%. The inks of two selected models were found homogenous within the ink reservoir. The HPTLC technique proved to be simple, reproducible (RSD<3%) and repeatable (RSD <3%).

Ref.- Borba et al. (2015). TI-Ball point pens (Blue) Raman spectroscopy , chemometrics Aim- Distinguish blue ball point pen inks Finding-The combination of Raman spectroscopy and chemometrics has proven to be useful to differentiate among different kinds of pen inks in complex multiclass problems.

Ref.-Ferreira et.al. (2015) TI-Ball point pen ink M d - Paper spray mass spectroscopy Aim-Forensic analysis of ballpoint pen inks using paper spray mass spectroscopy Finding-The new technique proved to be useful for analyżing documents and characteriżation of overlapped inks.

Ref.- Lee et al. (2016) TI- Ball point pens (Red) Md-Ultra high performance liquid chromatography (UPLC) A i m - Fast and simple forensic red ink analysis using UPLC Finding- Discrimination of 94.5% samples using 144 chromatograms by UPLC. UPLC is an effective technique than HPLC.

Ref.- Nunkoo, (2016) TI-Ball point pens black, 18 blue, 21 red and 15 green) Md-TLC, Infrared spectroscopy, visible spectroscopy, filtered light examination, ram a spectroscopy Aim-Forensic analysis of black, red, green, blue Finding-24 Black, 15 green, 21 red pens were succesfully discriminated by a combination of three techniques.

Ref.- Yadav, (2017) TI- Ball point pens (10 Blue) Md- Planar chromatography (paper&T LC). Aim- Analysis of commonly used blue ballpoint pen inks in India. Finding- Components of blueball point pen were not properly separated in paper chromatography, a proper separation is seen in TLC.

Ref.- Bansinge *et al.* (2018). TI- Ball point pens (12 Blue, Black, Red). Md-TLC, FTIR. Aim-Analysis of different ballpoint pen inks. TLC technique is complementary and very useful. Finding- Although FTIR is a well-established & non-destructive technique for the comparison of inks but not easy to discriminate these inks since all the samples have the same formulation.

Ref.-Copper et al. (2019). TI- Ballpoint pens. Md-Capillary electrophoresis. Aim- Analysis of ballpoint pen inks directly from paper. Finding- Direct sampling technique for capillary electrophoresis is a viable technique for the analysis of writing inks.

Ref.-Reference; TI- Types of Ink. Md-Methods employed. Aim- Aim of study. Finding- Output, results.

Conclusion

The technique of paper chromatography has been used to analyse ballpoint pen inks since 1950. Over time, alternative chromatographic techniques (TLC, HPLC,) have supplemented paper chromatography as effective procedures for the examination of ballpoint pens. Later, spectroscopic techniques (Raman spectroscopy, FTIR) and electrophoresis (capillary electrophoresis) emerged as tools for analysis that produced more trustworthy results than chromatographic procedures.

However, for the study of ballpoint pen inks, a combination of chromatography, spectroscopy, and electrophoresis proved to be the most effective method. Further analysis of ballpoint pens is needed.

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