Bulletin of Environment, Pharmacology and Life Sciences
Bull. Env. Pharmacol. Life Sci., Spl Issue [5] 2022 :299-303
©2022 Academy for Environment and Life Sciences, India
Online ISSN 2277-1808
Journal's URL:http://www.bepls.com
CODEN: BEPLAD

REVIEW ARTICLE **OPEN ACCESS**

A Review on Spectroscopic Techniques for Examination Of Ink

Mandeep Kaur Purba, Mehak Garg
Department of Forensic Science, Faculty of Science, SGT University, Gurugram, Haryana

ABSTRACT

Acquisition of modern values by documents is to deliver new objectives; it's plausible that they are turning into the medium of deceitful manipulation, the objectives of counterfeiting, or the instruments of camouflaging the truth.During the investigation of fraudulent documents, the composition of ink used can play a vital role in providing relevant and leading information.Determining the most effective and appropriate technique for examination ofinks is a challenging task. This review article focusses on the present and prospective applications of a variety of spectroscopic techniques for analysis of ink in questioned documents. The non-destructive nature of spectroscopic techniques makes them widely accepted and preferred tool for analysis of ink. Nonetheless, a combination of one or more spectroscopic techniques can provide more reliable results.

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

Received 22.10.2022 Revised 23.11.2022 Accepted 20.12.2022

INTRODUCTION

Humans' urge to share their thoughts with others led to the evolution of writing. Prior to the invention of visible signs that were easily understood by the general public, individuals communicated mostly through oral language. Finding good writing material was motivated by the desire to write [3]. The variety of writing tools has likewise changed over time. Chalk, graphite, pencils, crayons, various types of pens, etc. are examples of contemporary writing implements. Due to the adhesion or absorption phenomenon, writing can be observed on a piece of paper or any other surface. The main cause of the penetration of liquid writing ink is absorption [1-3]. Since many years ago, many procedures have been used for the study of various ink types.

Spectroscopic techniques used for ink examination

A technique is used to illuminate the ions with blue or green light and using an infrared sensitive film, infrared luminescence was recorded photographically. This technique is used to discriminate the ink constituents. By the absorbing a photon, the principle of excitation of the dye molecules to a higher energy level is investigated. In one or two mode, it returns to the ground energy level after a time period. Energy decay took place via thermal radiations in the first. After the emission of radiation, the excited molecule comes back to ground level in the other mode. By decreasing the temperature, the energy & frequency of molecular collisions were lowered. To increase the proportion of excited molecules decaying the emitting radiation, the intensity of luminescence was lowered as a result. To enhance the luminescence, liquid nitrogen was used to cool the inks on the document. It is done to make the ink decipherable [4].

In addition, a technique to differentiate dyes using infrared luminescence. This technique is non-destructive. For examining inks & based on the contents of infrared luminescent, the inks are classified into 3 groups. They are no luminescent dye constituents, dye constituent that luminesce and constituents some luminesced and other did not [24].

Micro spectrometry

Laing et al. (1983) Separation of dyes using chromatography from the thin layer to separate colour writing inks in the observed transmission or reflection spectrum of the individual components was then recorded. Studies have been carried out to find the effect of analysing different leaves. A miniature spectrophotometer is a device used to record spectra. Using a blunt hypodermic needle, a small circle of paper 0.5mm in diameter was finished with ink from the paper for the cart to charge with the soldiers. Also, by applying a drop of the medium of the xylene-based mixture, it is placed on a glass slide. Using a sharp scalpel, the ink fibbers were separated from the coloured paper by a magnifying glass, and then a cap was placed. In the reflection and transmission modes from 390 to 590 nm, the apparent spectrum was recorded. The deviations of the common absorption keys in more than one spectrum are large, and

deviations in the maximum absorption amplitudes and frequencies are observed when using the full spectra. The reverse method turned out to be very interesting because some examples where needed.
Due to tanning, the regenerated spectrum tested in reflection mode was low, e.g. it has a metallic pink sheen [25]. The deviations from the Beer-Lambert law due to the different models of diffusion, transmission and reflection of the paper were observed in a spectrum of inks obtained by micro-spectrophotometry [26].
Zeichner [30] concluded that regardless of this strategy, the results were ineffective. Attempts have been made to improve the strength of the micro-spectrophotometric solution if the ink on the coloured paper is used to analyze the ink on the paper. This is achieved by moving the gap of the inked wire in the holder, crushing it with a drill, or dipping it into the mounting bracket. To prevent breakage, some suitable pressure is applied to the glass slide during crushing. It has tried 10 blue and dark ballpoint pens. A fiber point pen and a ballpoint pen have also been tried. Pen inks were applied directly by loading or applying pressure to the slides in the glass slides. A small Docuspec TM / 1 mechanical spectrometer (Nano Measures Inc.) recorded all ink spectra. It includes the Olympus BHT magnifier with incandescent quartz LEDs. The starting frequency range is 380 to 764 nm. For those on white paper, the impact of the paper type on the purchased spectrum was examined by examining the spectrum recorded on the dust colour card. Blue and dark inks followed Beer-Lambert's law, and the results were given. The spectrum of unbroken bands of ink in glass is not the spectrum of stacked ink fibres. The pressure of a plane crash causes it. When the mash was broken up in the water and then dried, the results were reversed. An example of inkjet paper film stacked on a glass slide is more repetitive than the spectrum of ink fibres in the growing medium. If ink notes appear on coloured experimental paper, this is a personal advantage [30].
Direct analysis in real time mass spectrometry (DART-MS) was used for analysis of writing inks on paper. The spectrum was obtained for ball point, fluid and gel ink samples. They observed that the spectrum was affected if heavily processed papers were used. Even the age of ink depicted impact on the spectrum [15] .

Diffuse reflectance fourier transform infrared

Trzcińska, [27] has used Fourier Transform Infrared (FTIR) spectrometry to characterize the ink. Harris [13] proved that for analysing paper fibres saturated with inks, its use of micro-reflectance spectroscopy & diamond cell transmission are not successful. Diffuse reflectance (DR) FTIR is believed to be a non-destructive analysis for ink on paper and also reliable as per scientists.Comparison of known pink inks and their known reference spectrum does not erase the spectrum acquired by ink on paper by Herris. It studying of ballpoint ink reflection and diffuse reflection on paper with the FTIR microscope. Along with it, Fuller & Griffiths [9] used DR to isolate samples by TLC and FTIR evaluation. Further, Suzuki & Gresham (1986) focused on the screening of solids using DR with FTIR. From models directly protected in response to KBr, these can provide the correct spectrum transparently.
Merrill et al. [20] produced a library of accessible scattering reflection spectra using FTIR programming. The colours, tones and areas of the various compounds recorded in the paper text and the ink concentration of the ballpoint pen are verified using the FTIR spectrum of known ink samples. The separation can damage inks from different manufacturers. Since TLC cannot detect it, tar can be determined using a product capable of suppressing the spectrum (Merrill & Edward, 1992).Studies show that colour Xerox reports designed using the FTIR Partial Absorption Spectrum (micro RAS-FTIR) are undoubtedly different from previous ones. This technique is one of the most dangerous approaches to consider in shadow guided recordings (Sarin et al., 1999)
Harada studied 74 scrutinized liquid and oil inks using 4 techniques. They were photographed before and after opening under UV light, marked light and TLC. It was detected by densitometry, X-ray microbiological examination and observed spectrophotometry. The black ink is the result of the invention of the brand. The criminal complaint was filed using the above official combination(Harada, 1988).
108 blue ink samples were classified by FTIR spectroscopy, and the presence of key stabilizers were analyzed. The spectral properties of inks were illustrated by the arithmetic inference of recognition of examples, e.g. Frequency and absorption and 35 subgroups are recognized by the connection coefficient (λ). A method has been obtained to improve the duration of exposure to heat or ultraviolet rays of inks [26]. In addition, ballpoint pen inks mainly extracted from paper were separated using the UV-visible spectrum in the 400nm-700nm range [29].
Amador et al. [1] explored the function of advanced ballpoint pen ink using paper mass spectrometry (PS-MS). The inks differ in the design of their branded products derived from 6 different brands. After opening the luminaire, PS-MS with Partial least Squares (PLS) was used to study the progress of the arrangement of ink materials. In 3 different applications, the measurement of the developed method has also been demonstrated in scientific experiments. These include the analysis of old inks, the analysis of new closed ink lines, and the reconstructed tradition's discovery.

Kumar & Sharma (2017) investigated component measurements with destructive UV-visible (ink-dissolving) spectroscopy using chemical and broad-spectrum non-reflective UV-Vis-NIR measurements. To determine the ink spectral reflections between the same and different products, 57 blue ballpoint pen ink samples were cut under optimal conditions. Primary component analysis (PCA) and K information sequence analysis were used to determine whether UV-Vis / UV-Vis NIR spectra could distinguish the blue inks of ballpoint pens. Using the analysis of the optical spectrum (absorption peaks), the calculation of the separating force of the destructive and non-destructive modes was supplemented by an automated analysis. They found that the metric chemo method gave better separation forces (98.72% and 99.46%, non-destructive and non-destructive, separately) compared to the instrumental analysis (69.67%) [14].

Luminescence photography

Kirchner [15] used another method to thin-layer chromatography and identifiable ink. Optical imaging has been used to report fractions derived from thin-layer chromatography, Luminescence photography as it is the most sensitive method (Kirchner & Justus, 1978).Use 100 different ink values by micro layer chromatography using various soluble structures such as the eluent and tapping their fractions. It made ink colors become a more reliable target. CH3) 2CO and pure water (85:15 v / v) were used for the ballpoint pen inks 0.88 alkaline water (99: 1 v / v) has been used for dark inks and non-ethyl alcohol [19].

Laser excitation and spectroscopy

Sinor et al. [25] examined questioned documents & distinguished inks visually via laser-induced fluorescence with the help of optical spectroscopy & lasers. It was sufficed by photographic documentation of the case in those circumstances & to contemplate spectroscopic measurements, none is required. Comparative inks were not significantly separated by visual inspection under laser stimulation. Three methods are used: thin layer chromatography, micro-spectrometry and infrared fluorescence. Sinor and his colleagues inspected 30 ballpoint pens and permeable tip pens with black, blue and red highlight inks. The absorption spectrum was activated using the Perkin-Elmer 356 spectrometer as an instrument. Using the Ar 5145 laser stimulus, infrared incandescent images were recorded for the following experiment. The thin sheet is chrome plated with a glass plate of 100% C-18 silica gel. The separating agent is a mixture of methanol, CH3) 2CO and purified water equivalent. By detection, ink tests were used. The sensitivity can be greatly improved by using the existing laser stimulation to separate the dyes from the DLC plates. For example, when the temperature of liquid N2 decreases, there is an expansion of the light output, which is explained in more detail. Small differences that a song expects in a particular example, rather than the actual sequence, are usually considered by my plots based on their findings. A small spectral asymmetry should not be considered a precursor of stamping ink patterns.

Raman spectroscopy

Fabianska and Trzcinska [7] used 4 techniques to distinguish between ballpoint and liquid inks. They analysed samples using Raman spectroscopy, TLC under visible and infrared light, along with IR spectroscopy and MK-FTIR. The results showed that Raman spectroscopy could serve as an alternate to optical method. However, they concluded that destructive methods are still required for analysis of ink .

Furthermore, Geiman et al. [10] study dyes produced in ball inks by material optimization from Raman spectroscopy and Raman Scattering Surface Improvement (SERS). The FT frame (1064nm laser) is used to obtain a spectrum of 10 pigments under various scientific conditions, for example, TLC points based on high brightness, powder and compound coolers, and the most intense spectrum quality described as the standard Raman Diffusion (laser 633 nm, 785 nm). SERS has proven to be effective. The transparent forensic implementation of the strategy by improving ball point ink and its color rules will be displayed on the TLC panel.

Kunickiin [17] evaluated the sharing strength between different techniques using ballpoint pen inks using Raman spectroscopy, optical techniques and TLC techniques. Appropriate extracting solvent is found to be an essential element of his evaluation. A well differentiated chromatogram is produced by developing solvent systems.

e Brito et al. [6] analyzed the crossed lines by evaluating the potential of the intense infrared spectrum associated with diverse data analysis. Adjacent Infrared Hyper spectral Imaging (HSI-NIR) is used in conjunction with multidimensional data analysis for non-destructive, rapid and objective linear cross-sections of dark pens. Twenty-one black and dry gel pens of various products and designs were used to set up the bifurcated summary on white office paper. Primary component analysis (PCA) and minimum squared analysis (PLS-DA) were used to determine the key factors. The source spectrum and the preset spectrum construct the frame flange structure in Multilayer Curve Resolution Minimum Squares (MCR-ALS). Evidence of pixel misalignment in ink rotation maps is the result of post-processing of the pre-processing spectrum. An accurate guarantee for crossover orders at a set of gel-pen junctions is provided by the MCR-ALS series using Raw Spectra. The rest of the commands performed by removing a spot of ink

from the pen may result in erroneous or difficult separation of the ink paper. The operational advantages of the HSI-NIR were illustrated by the results obtained even though various chemical measurement methods are considered to have exceeded a fraction of the spectral limits at their conclusion, with record evaluation and difficulties in applying this result in real cases of forensic medicine.

Costa et.al (2019) used correlation analysis and direct injection mass spectrometry to estimate the recorded ink color time. The ULT (Unauthorized Limit) method makes it possible to estimate the archiving date of the originals considered and analyze the ballpoint pens' inks. Training tests were omitted from major forensic reports published between 1962 and 2014 to confirm designs for long-term ink damage. A large species were captured in the long-distance ink program when examining the 505 Electronic Spray Ionization Mass Spectrometry (ESI) tests. The ULT method was used to analyse the relationship between ink compounds using the cosine amplitudes to compare the upper parts of static mass spectrometry. For each type of identification defined, this method allowed a strong, basic and rapid evaluation of the margin relation and my dating extensions. Depending on the composition of the compound (methyl or ethyl) lost in the corruption cycle, there may be an abnormal change in colour integrity when viewing. Previous information about objects, for example, storage conditions or the start of the description of colors, does not depend on how their original nature created them. Since this type of data is generally not available to forensic experts, this component may be useful in actual forensic applications of their choice [5].

Researchers analysed inks in questioned documents using Raman spectroscopy. The issue of intersecting lines & chemistry of ink-paper interactions are focused by them (Braz et al., 2013). Additionally, Silva *et.al.* (2014) differentiated black pen inks of various brands, types & models for cursive handwriting with a method proposed by them. To obtain reflectance spectra and differentiation of inks, VSC 6000 was used which was done using partial least squares (PLS-DA). Low root mean squared error of predictions (RMSEPs) is presented by PLS-DA models. Effective, non-destructive & rapid differentiation of all pen inks was permitted. For identification of pen type, brand & model in case of questioned document examination, this method is useful as per their conclusion (Silva et al., 2014).

da Silva Ferreira *et.al.* [8]) analysed ballpoint pen inks using a novel analytical technique paper spray mass spectrometry (PS-MS). They analysed inks under ambient conditions. Typical profiles were obtained on analysing pens from different brands, further changes in ink composition were also analysed in PS-MS. This new technique proved to be useful for analysing documents and characterization of overlapped inks [8].

CONCLUSION

Determination of the best and appropriate techniques for examination of inks is a tedious task. The variation in composition of inks can play a crucial role in establishing the authenticity of a document. Since decades, spectroscopic techniques have demonstrated to be sophisticated and widely accepted non-destructive techniques for comparison of inks on handwritten documents. However, in certain cases, a combination of spectroscopic and other techniques such as chromatography, electrophoresis etc. have been effectively used for analysis of inks. Nevertheless, spectroscopic studies for ink analysis will continue to complement forensic examiners with the present workflow of questioned document examination to provide qualitative as well as quantitative data.

REFERENCES

1. Amador, V. S., Pereira, H. V., Sena, M. M., Augusti, R., & Piccin, E. (2017). Paper Spray Mass Spectrometry for the Forensic Analysis of Black Ballpoint Pen Inks. *Journal of the American Society for Mass Spectrometry*, *28*(9), 1965–1976. https://doi.org/10.1007/s13361-017-1686-z
2. Braz, A., López-López, M., & García-Ruiz, C. (2013). Raman spectroscopy for forensic analysis of inks in questioned documents. *Forensic Science International*, *232*(1–3), 206–212. https://doi.org/10.1016/j.forsciint.2013.07.017
3. Brunelle, R. L., & Crawford, K. R. (2003). *Advances in the forensic analysis and dating of writing ink*. Charles C. Thomas. http://public.ebookcentral.proquest.com/choice/publicfullrecord.aspx?p=605194
4. Brunelle, R. L., & Reed, R. W. (1994). *Forensic examination of ink and paper*. C.C. Thomas.
5. Costa, K., Brand, G., Groberio, T., Braga, J. W. B., & Zacca, J. J. (2019). Document ink dye age estimation by direct injection-mass spectrometry and correlation analysis. *Microchemical Journal*, *149*, 1123–1132. https://doi.org/10.1016/j.microc.2019.04.034
6. e Brito, Braz, A., Honorato, R., Pimentel, M., & Pasquini, C. (2019). Evaluating the potential of near infrared hyperspectral imaging associated with multivariate data analysis for examining crossing ink lines. *Forensic Science International*, *298*, 169–176.
7. Fabiańska, E., & Trzciñska, B. M. (2001). *Differentiation of ballpoint and liquid inks – a comparison of methods in use*. Problems of Forensic Sciences, XLVI, 383-400.

8. Ferreira, P. da S., Silva, D. F. de A. e, Augusti, R., & Piccin, E. (2015). Forensic analysis of ballpoint pen inks using paper spray mass spectrometry. *Analyst*, *140*(3), 811–819. https://doi.org/10.1039/C4AN01617C
9. Fuller, M. P., & Griffiths, P. R. (2002). *Diffuse reflectance measurements by infrared Fourier transform spectrometry*. ACS Publications; American Chemical Society. https://doi.org/10.1021/ac50035a045
10. Geiman, I., Leona, M., & Lombardi, J. R. (2009). Application of Raman Spectroscopy and Surface-Enhanced Raman Scattering to the Analysis of Synthetic Dyes Found in Ballpoint Pen Inks*. *Journal of Forensic Sciences*, *54*(4), 947–952. https://doi.org/10.1111/j.1556-4029.2009.01058.x
11. Harada, H. (1988). A rapid identification of black colour materials with specific reference to ballpoint ink and Indian ink. *Journal of the Forensic Science Society*, *28*(3), 167–177. https://doi.org/10.1016/S0015-7368(88)72826-1
12. Hardcastle, R. A., & Hall, M. G. (1978). A Technique for the Enhancement of the Infra Red Luminescence of Inks. *Journal of the Forensic Science Society*, *18*(1), 53–55. https://doi.org/10.1016/S0015-7368(78)71182-5
13. Harris, J. (1991). A Preliminary Report on the Nondestructive Examination of Ballpoint Pen Ink on Questioned Documents by FT-IR Spectroscopy. *Canadian Society of Forensic Science Journal*, *24*(1), 5–21. https://doi.org/10.1080/00085030.1991.10756979
14. Jones, C. M., & Fernández, F. M. (2013). Transmission mode direct analysis in real time mass spectrometry for fast untargeted metabolic fingerprinting. *Rapid Communications in Mass Spectrometry*, *27*(12), 1311–1318. https://doi.org/10.1002/rcm.6566
15. Kirchner, & Justus, G. (1978). *Thin Layer Chromatography. 2nd Ed by Kirchner, Justus G:* https://www.abebooks.com/9780471932642/Thin-Layer-Chromatography-2nd-Kirchner-0471932647/plp
16. Kumar, R., & Sharma, V. (2017). A novel combined approach of diffuse reflectance UV–Vis-NIR spectroscopy and multivariate analysis for non-destructive examination of blue ballpoint pen inks in forensic application. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *175*, 67–75.
17. Kunicki, M. (2002). Differentiating blue ballpoint pen inks. *Z zagadnien nauk sadowych , LI, 56-70.*
18. Laing, D., & Issacs, M. (1983). The Comparison of Nanogram Quantities of Ink Using Visible Microspectrometry. *Journal of Forensic Sciences*, *23*, 147–154.
19. LaPorte, G. M., Arredondo, M. D., McConnell, T. S., Stephens, J. C., Cantu, A. A., & Shaffer, D. K. (2006). An Evaluation of Matching Unknown Writing Inks with the United States International Ink Library. *Journal of Forensic Sciences*, *51*(3), 689–692. https://doi.org/10.1111/j.1556-4029.2006.00144.x
20. Merrill, R., & Edward, E. (1992). Analysis of Ballpoint Pen Inks by Diffuse Reflectance Infrared Spectrometry. *Journal of Forensic Sciences*, *37*(2), 528–532.
21. Moody, C. M. (2010). *Black Writing Ink Analysis By Direct Infusion Electrospray Mass Spectroscopy*.
22. Sarin, R., Rasool, S., Krishna, M., & Mehrotra, V. (1999). Forensic Examination of Forged Colour Xerox Documents by Micro-Ras FTIR Spectroscopy. *Journal of Forensic Document Examination*, *5*, 265–269.
23. Sensi, C., & Cantu, A. (1982). Infrared Luminescence: Is It a Valid Method To Differentiate Among Inks? *Journal of Forensic Sciences*, *27*, 196–199.
24. Silva, V. A. G. da, Talhavini, M., Zacca, J. J., Trindade, B. R., & Braga, J. W. B. (2014). Discrimination of Black Pen Inks on Writing Documents Using Visible Reflectance Spectroscopy and PLS-DA. *Journal of the Brazilian Chemical Society*. https://doi.org/10.5935/0103-5053.20140140
25. Sinor, T., Jeffery, P., Everse, K., & Menzel, E. (1986). Lasers and Optical Spectroscopy in Questioned Document Examination. *Journal of Forensic Sciences*, *23*, 825–839.
26. Suzuki, E., & Gresham, W. (1986). Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): I. Principles, Sampling Methods, and Advantages. *Journal of Forensic Sciences*, *31*(3), 931–935.
27. Trzcińska, B. M. (2001). Analysis of writing inks in changed documents: A preliminary study with thin layer chromatography. *Chemia Analityczna*, *Vol. 46, No. 4*, 507–513.
28. Wang, X.-F., Yu, J., Xie, M.-X., Yao, Y.-T., & Han, J. (2008). Identification and dating of the fountain pen ink entries on documents by ion-pairing high-performance liquid chromatography. *Forensic Science International*, *180*(1), 43–49. https://doi.org/10.1016/j.forsciint.2008.06.008
29. Zaharullil, N. A., & Ahmad, U. (2012). Discrimination of Ballpoint Pen Inks Using Spectroscopic Methods. *Undefined*.https://www.semanticscholar.org/paper/Discrimination-of-Ballpoint-Pen-Inks-Using-Methods-Zaharullil-Ahmad/057caa7896e60e3506fe8a4ad45395e637b5451d
30. Zeichner, A., Levin, N., Klein, A., & Novoselsky, Y. (1988). Transmission and Reflectance Microspectrophotometry of Inks. *Journal of Forensic Sciences*, *33*, 1171–1184. https://doi.org/10.1520/JFS12551J

CITATION OF THIS ARTICLE

Mandeep Kaur Purba, Mehak Garg :A Review On Spectroscopic Techniques For Examination Of Ink. Bull. Env.Pharmacol. Life Sci., Spl Issue [5]: 2022: 299-303.