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DETECTION AND IDENTIFICATION OF PRINTER INKS - A REVIEW REPORT ON LASER AND INKJET PRINTER INK ANALYSIS

Rashmi Sharma[1], T.R.Baggi[2], Amit Chattree[3], Lav Kesharwani[4], A.K.Gupta[4]

[1]Central Forensic Science Laboratory, Ramanthapur Hyderabad, India
[2]Forensic Science Unit, Department of Chemistry, University college of Science, Osmania University, Hyderabad, AP, India
[3]Department of Chemistry, Sam Higginbottom Institute of Agriculture, Technology and Sciences, Allahabad, U.P., India
[4]Department of Forensic Science, Sam Higginbottom Institute of Agriculture, Technology and Sciences, Allahabad, U.P., India

E-mail of Corresponding Author: rrashmi_amity@yahoo.com

ABSTRACT

The increased rate of crime involving the use of laser and inkjet printed documents is the motivation of writing this paper and to produce efficient analytical techniques for classification, identification, detection and analysis of laser and inkjet printed documents. A printed document is usually examined to determine whether or not it is forged or to determine its source of origin etc. The examination can be carried out either physically and chemically. The main aspiration of this paper is to collect and provide every useful and relevant information so that they can be implemented in a questioned document laboratory. This review paper indicates how the analysis of the printer inks can be used for the establishment of origin of a printed document.

Keywords: laser and inkjet printer, analytical techniques, ink analysis

INTRODUCTION

The technology of inkjet and laser printing has spread in past few decades and continue to develop due to the quality of print, reduced cost of inkjet and toner printers. The printers based on the laser and inkjet technology have occupied a strategic position for the commercial and personal use and thus are a target for criminal activities. With the increased number of forgeries involving printed documents there is a need of development of techniques which can help in detection of crime involving the printed documents. The investigations must be led as possible by minimizing the destruction of the questioned documents. Many publications make reference to the forensic analysis of printing ink (laser printer toner and inkjet ink) involving both destructive and non destructive examination.

The scientific basis of all papers, presentations and posters isn't validated by the authors of this review, as high number of references from the variety of sources was collected. This paper is essentially based on articles published in the major forensic science journals as well as presentations or posters presented at international forensic meetings to some extent. Many publications are available which describes the analytical methods giving information on the composition of these inks. The number of existing information and papers that can be useful for document examiners is huge. Although we tried to cover maximum number of information on the analysis of toner and inkjet ink still some lacks or omissions are possible.

This paper aims to provide an in-depth review of the technical advances in the field of laser and inkjet ink analysis. The main aim of this paper is

to help FDE to choose good technical orientations for the examination and for the further development of the techniques. Keeping in consideration the need for printer ink analysis to fight against the forgeries involving printed documents many authors have given their contribution to this field which has briefly described below:-

Heuser (1987) used SEM-EDX for the analysis of photocopy toners and found the technique to be very useful in recognizing monocomponent process toners as they contain a magnetic carrier material usually magnetite that is detectable by this type of analysis. He was able to differentiate easily between mono component and dual component process toners, because the dual component process does not result in magnetic carrier is continually recycled. Although Heuser was able to easily identify the presence of iron in some toner samples, interpretation of additional inorganic constituents was difficult due to the interference produced by the paper background.

Aginsky (1993) employed the ascending mode thin layer chromatography technique using a multiple development procedure. The purpose of study was to separate coloured components of computer printing Inks, artist's paints, copier toners, and colour pencils. The procedure used was able to separate pthalocyanine pigments and slightly soluble organic pigments. He analyzed 120 synthetic pigments and dyes used for commercial production of modern artist's paints, toners for copying machines, printing and writing inks by TLC. After TLC the sample was taken by scratching writing material using razor and extracted by dimethylformamide. The three step TLC procedures were proved to give valuable information about inks, coloured organic components including the sparingly soluble ones.

Espadaler et al (1993) analyzed the organic and inorganic ink components of ink using the GC-MS and SEM-EDX respectively in order to explain the acidic behaviour and permanence of black colour in some inks. The inorganic components are the iron and copper sulphates. Their preparation is based on tannin extraction, with which the iron that yields the iron sulphate forms a black suspension that is retained and thickened by the gum arabic. One of the most important causes of degradation in ancient manuscripts is the acidity ink. The relationship between the important corrosion that some inks incite in the support and the fact that a strong black colouring remains in the ink has often been demonstrated. By contrast, no acidity is shown in light coloured or slightly dark inks.

Andrasko (1994) discussed a sampling technique using the metallic stubs for the removal of photocopy toner from the photocopied document by thermal transfer. The technique is simple and cause negligible destruction to the document. The toner samples were then analyzed by micro reflectance FTIR. The technique shows good reproducibility, is sensitive and applicable to small areas on the transferred material.

Jasuja et al (1997) analyzed different 20 green, blue, and red offset printing inks from Thin Layer Chromatography. The 5 sq mm sample of these inks was taken from the documents and extracted the ink from paper with few drops of mixture of pyridine and glacial acetic acid (3: 1). Studies reported that the number of spots, colour and Rf values inks could be taken into consideration for the differentiation of ink using TLC. They also reported different solvent systems for different colours of ink.

Doherty (1998) compared and studied ink samples from current and discontinued inkjet printer models for the classification and dating the formulations of ink. The black samples printed with 18 types of cartridges and unprocessed samples from 8 black ink cartridges were analyzed for their physical & chemical properties. The authors reported methanol and water (1: 1) as best solvent to dissolve ink from the printed document. They concluded that (a) processed and raw inks from the same model cartridges produced

consistent chemical and different spectral results (b) many of the inks could be differentiated and classified and (c) the limited sampling of inks available for dating could be correlated to their respective introduction or reformulation date.

Pagano et al (2000) reported the separation of components of cyan, magenta, yellow and black inks after extracting with the solvent ethanol/water (1:1).Studies reported that ethyl acetate:ethanol:water(70:35:30) and water: acetic acid:butanol:butyl acetate(32:17:41:10) were the best solvent systems for separation of ink components. Authors suggested the creation of library with database of various original and refilled inks chromatograms will be helpful for the matching of the questioned inks with the standard inks. Besides, the authors also described the inkjet printing technology along with the composition of inkjet ink analyzed.

Sidhu et al (2000) analyzed 22 black and 17 colour ink writing samples of various models of inkjet printers using thin layer chromatography. The research concluded the samples of black and coloured inks could be separated and differentiated from each other. The solvent systems butanol:propanol: water(80:15:5) and butanol:ethanol:water (50:15:5) were found suitable for for the separation of black ink, whereas for the coloured inks the solvent systems butanol:propanol:glacial acetic acid (60:15:05) and chloroform:methanol: n-Hexane:Glacial Acetic Acid (70:20:5:0.5) were found most suitable.

Anglos et al (2001) reported the origin (and date of first use) of inorganic pigments as used in archeological inks, paints, and prints. The list of pigments also provides the elemental composition associated with a given pigment (i.e. Egyptian blue = CaCuSi4O10 and Naples yellow = Pb2Sb8O7, etc). From these pigments elements like Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Na, Pb, Sb, Se, Si, Sn, Sr, Ti, and Zn can be derived as the possible elemental composition. Laser Induced Breakdown Spectroscopy(LIBS) spectra for a group of the pigments has also been reported, although such spectra reported the basic pigment and not the pigment as part of an ink matrix where it will certainly be diluted by the other ink components would potentially more erratic LIBS spectra as compared the "clean" spectra presented in the reported work.

Merrill et al (2003)-I reported microscopical reflection absorption by infrared spectroscopy as a viable technique for analyzing the polymer resins contained in dry black photocopy and printed toners. The sampling technique involves a heat transfer of the toner from a document to the reflected surface of aluminum foil followed by analysis by R-A IR. The technique is fast, reliable and easily available to many forensic science laboratories. A searchable library was created that contains 807 toner samples analyzed by R-A IR.98 groups were establish based on spectral characteristics and a flow chart was developed to assist with group assignments. A blind study was conducted to compare 20 photocopied documents each paired to a test document to determine if the pair could have been produced from the same copier. The analyst obtains 100%
correct result in this study. Tests on 30 samples with the spectral library produced 90% first hits for the correct group. The three remaining samples were correctly determined by visual comparison of spectra for the top three hits. An actual case study was conducted where the investigation was narrowed from 400 possible machines to 8 based on a comparative study based on the photocopy toners.

Merrill et al (2003)-II utilized the reflection-absorption infrared microscopy (R-A-IR) technique for the analysis of copy toner samples. The copy toners were grouped into distinguished classes on visual comparison and computer assisted spectral matching and was then compared to that achieved by multivariate discriminant analysis. Out of data set of spectra of 430 copy toners, 90% (388/430) of the spectra were initially correctly grouped into the classifications previously established by spectral matching. Three

groups of samples that did not classify well contained too few samples to allow reliable classification. Samples from two other pairs of groups were similar and often misclassified. Closer examination of spectra from these groups revealed discriminating features that could be used in separate discriminant analyses to improve classification. For one pair of groups, the classification accuracy improved to 91% (81/89) and 97% (28/29), for the two groups, respectively. The other pair of groups were completely distinguishable from one another. With these additional tests, multivariate discriminant analysis correctly classified 96% of the 430 R-A IR toner spectra into the toner groups found previously by spectral matching.

Merrill et al (2003)-III analysed copy toner samples using scanning electron microscopy with X-ray dispersive analysis (SEM-EDX) and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS).the samples analysed were differentiated into 13 subgroups based on Principal component and cluster analysis of SEM data for 166 copy toners. The basis of grouping was the presence or absence of a ferrite base. When toners were compared for which both SEM and reflection-absorption infrared spectral data were available, 41% of the samples could be assigned to specific manufacturers. Py-GC/MS on poly (styrene:acrylate)-based toners produced eight peaks relevant to toner differentiation. One third of the toners clustered in a small group that contained five statistically different subgroups. Of the 57 toners for which both Py-GC/MS and SEM data were available, 31 could be differentiated using the combined analytical results. The synergy of the complementary information provided by Py-GC/MS and SEM narrows matching possibilitis for forensic investigations involving copied or laser printed documents.

Rasool et al (2004) successfully utilized the technique of micro-reflectance absorbance FTIR to differentiate the original and duplicate of inkjet printer ink cartridges on comparing the chemical composition of ink. On the basis of a comparison of spectra generated by micro-reflectance FTIR the original inkjet cartridge ink can be characterized and assigned representative fingerprint spectra.

Trzcinska (2006) classified 162 samples from 82 different types of cartridges produced by 21 manufacturers using fourier transform infrared spectroscopy and X-ray fluorescence spectrometry. They reported that if two samples are similar in polymer composition XRF analysis may discriminate both of them. The author successfully utilized the FT-IR technique and XRF to differentiate 82.5% and 90.8% pairs of examined samples.

Fittschen et al (2008) made use of LA-ICP-MS for the analysis of inkjet printer inks. Picoliter droplets of ink (HNO3 spiked with As, Co, Fe, and Ti) were delivered from an ink-jet printer onto acrylic glass, allowed to dry, and then analyzed. The technique proved to offer a potential quantification analysis for ink, provided that a matrix-matched standard can be produced.

Donnelly et al (2009) analysed inkjet inks by Laser Desorption Mass Spectroscopy to determine the number of inks used by a printer and the chemical composition of the colorants.

LaPorte et al (2009) used Direct Analysis in Real Time – Mass spectrometry (DART™ -MS) methodology for the identification of coloured inkjet ink. The technique is virtually non-destructive, involves very little sample preparation and allows creation of a spectral searchable database.

Szafarska et al (2009) emphasized on the chemical analysis of inkjet printer inks due to the wide spread extensive use of inkjet printers .He used the capillary electrophoresis technique, with simplified stages of extraction to differentiate between inkjet inks.

DISCUSSION

From the review of the researches discussed in this paper we can say that the examination of a printed document conventionally consist of the examination of the document for the indication of particular make or model of machine used which can be further improved by examination of them for their chemical characteristics by using various instrumental methods and finally their comparison with the standard document to identify the source of origin. Very less work has been reported in India on the examination of laser or inkjet printed document. There is a need to systemically work on the problem by employing various chromatographic, spectroscopic, computerized and other techniques to achieve good discrimination between printed documents.

CONCLUSION

The document examination expert now has an array of techniques such as chromatography (TLC, HPTLC,PyGC,HPLC),Spectroscopy(FT-IR,SEM-EDX,LDMS) for the analysis of ink including opining on the printer source of suspected document, to compare the suspected document with the admitted printed specimen, for the elimination or inclusion of suspected printer in the investigation etc. besides all these there is a need to develop ink libraries and to update them time to time along with the development in the printer ink advancements. The investigation of ink for the ink composition with the more sensitive and advanced techniques such as ICP-MS is required. Image processing of spectrum obtained by various instruments such as FT-IR could be a helpful approach for the comparative analysis of ink.

This is a need of the hour that image processing tools should be developed and be successfully employed for the discrimination of inks as reported by Djozen. The authors developed software in MATLAB based on the intensity profile of RGB characterstics for the discrimination of pen inks after TLC analysis. Such tools can successfully be employed for the examination of printing inks also.

REFERENCES

1. Heuser HG. Methods concerning classification and identification of photocopies. In proceedings of International Symposium on Questioned Documents. Federal Bureau of Investigation: 1987; Washington DC.
2. Aginsky VN. Comparitive Examination Of Inks by Using Instrumental thin layer Chromatography and Microspectrophotometry. Journal of Forensic Science JFSCA. 1993; 38(5):1111-1130.
3. Espadaler I, Sistach MC, Cortina M, Eljarrat E, Alcaraz R, Cabañas J, Rivera J. Organic and Inorganic Components of Manuscript Inks. ICOM Committee for conservation.10th Treennial meeting Washington,DC,USA. 1993 August 22-27.
4. Andrasko J. A simple method for sampling photocopy Toners for Examination by Microreflectance Fourier Transform Infrared Spectrophotometry. Journal of Forensic Sciences JFSCA.1994; 39(1):226-230.
5. Merrill, R.A., Bartick,E.G.,and Mazzella ,W.D.,"Studies of Techniques for Analysis of Photocopy Toners by IR," journal of Forensic Sciences, JFSCA, Vol.41,No.2,March 1996,pp.246-271.
6. Jasuja OP, Sharma R. Thin layer Chromatographic Analysis of Some Printing Inks. International Journal of Forensic Document Examiners. 1997; 3(4):356-359.
7. Doherty P. Classification of Inkjet Printers and Inks. Journal of the American Society of Questioned Document Examiner. (1998). 1(2): 88-106.
8. Pagano LW, Surrency MJ and Cantu AA. Inks: Forensic Analysis by Thin Layer (Planar) Chromatography. Encyclopedia of separation science. 2000; 7: 3101-3109.
9. Sidhu TK.Thin Layer Chromatographic Analysis of Inkjet Printer Inks. A Report

submitted to Punjabi University, Patiala (Unpublished Work).

10. Anglos D. Applied Spectroscopy 2001; 55:186-205A.
11. Merrill RA,Bartick EG,Taylor JH III.Forensic discrimination of photocopy and printer toners, part I. Anal Bioanal Chem 2003;376:1272-8.
12. Merrill RA,Bartick EG,Taylor JH III.Forensic discrimination of photocopy and printer toners, part II Anal Bioanal Chem 2003;376:1279-85.
13. Merrill RA,Bartick EG,Taylor JH III.Forensic discrimination of photocopy and printer toners, part III Anal Bioanal Chem 2003;376:1286-97.
14. Rasool SN, Varshney KM, Sudhakar P. Forensic Examination of ink in inkjet printer cartridges by FT-IR-Micrscopy. The forensic Scientist OnLine Journal, 2004; 7: 1-7.
15. TrZcinska BM. Classification of Black Powder Toners on the Basis of Integrated Analytical Information Provided by Fourier Transform Infrared Spectrometry and X-Ray Fluorescence Spectrometry. Journal of Forensic Science. 2006; 51:4
16. Fittschen UE, Bings NH, Hauschild S, Forster S, Kiera AF, Karavani E, Fromsdorf A, Thiele Anal Chem J. 2008; 80:1967-1977.
17. Donnelly S, Marrero JE, Cornell T, Fowler K, Allison J. Analysis of pigmented inkjet printer inks and printed documents by laser desorption/mass spectrometry. Journal of Forensic Science. 2009; 55(1):129-135.
18. LaPorte GM, Wilson JL, Houlgrave SM, Stephens JC. The classification of inkjet inks using accuTOF DART (Direct Analysis in Real Time) mass spectrometry. American Academy of Forensic Sciences -Denver - 2009, XV (J17).
19. Szafarska M, Solarz A, Poluszny RW, Wozniakiewicz M, KoscieIniak P. Optimization of extraction of inkjet inks from paper for forensic purposes .5th European Academy of Forensic Science Conference.2009; QD 05.