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Laser-induced breakdown spectroscopy (LIBS) for printing ink analysis coupled with principle component analysis (PCA)

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Abstract. Laser-induced breakdown spectroscopy (LIBS) has been applied to perform elemental analysis of printing ink samples. Samples of black printing inks from three types of printers *viz.* inkjet, laser-jet, and photocopier (three different brands for each type) and one control sample (blank white A4 paper) were analysed under optimised conditions. Results revealed that the LIBS method when coupled with PCA was able to provide discriminative evidence on elemental differences among all the different printing inks. Considering its time and cost effectiveness as well as requiring only minute amount of sample with no sample pre-treatment steps, the combination of LIBS and PCA may prove useful for forensic questioned document practical caseworks.

INTRODUCTION

The high degree of verisimilitude for forged documents has drastically increased due to the rapid improvement of computer hardware, software and high-quality printers [1], coupled with malicious intentions driven by multifactorial factors such as job demands, self-esteem, under financial strain, and pressure for other parties [2]. Putting into perspective, fraudulent activities such as faking police and/or medical reports, wills, certificates, counterfeited bank notes, and letters may carry significant repercussions that may prove detrimental for societal well-beings. Given such importance, the ability for detecting forged documents requires continuous empirical studies, capitalising on the forefront of scientific endeavours for ensuring the admissibility of the evidence in the court of law.

Standard techniques that used for the forensic examination of ink started with non-destructive optical examination (i.e. light microscope) followed by thin layer chromatography (TLC), gas chromatography (GC-MS, Pyr/GC-MS), high performance liquid chromatography (HPLC), capillary electrophoresis (CE, CE-MS), X-ray fluorescence (XRF), and micro spectrophotometry [3]. The majority of the proposed techniques are destructive in

natures and more appropriate for the identification of the organic profile of inks. The destructive chemical method seems to be unfavourable in forensic context due to the limitation in the availability of the forensic evidence. As such, a nearly non-destructive technique is needed for forensic examination of inorganic part of printing ink.

The elemental analysis becomes a more important tool for characterization and discrimination of inks with the stand of different manufacturers may use varying compositions of inorganic materials for producing ink, and its quantitation may lead to the possibility of identifying the unique chemical fingerprint for each manufacturer. In addition, the process of ink formulation may expose to other contamination of raw materials. With the standard protocol of forensic examination of inks, the elemental analysis is not widely used in the routine of examination.

The diversity in elemental composition in printing ink is resulted from various printing mechanism. The inkjet ink is in the form of liquid mostly made up of pigments and extenders, dyes, oils, resin, solvents, driers as well as plasticisers and other additives [4]. It is totally difference for toners which is in the form of finely grounded power with major components of polymer, colourant, external additives and charge control agent (CAA) [5-7].

Elemental analysis of inks can be done using XRF, LA-ICP-MS, micro-PIXE, and LIBS. The listed methods were mostly employed to study historical and artistic prints rather than forensic context [8-11]. However, recently LIBS and LA-ICP-MS are often used for forensic examination [12-15]. The laser-based methods allow fast and direct analysis of the sample with no or minor sample preparation.

To discriminate or identify the differences, often, comparative study is used. Hoehse *et al.* [16] had employed PCA, SIMCA and PLS-DA for classification of pigments and inks using combined Raman spectroscopy and LIBS. The techniques with multivariate analysis for ink analysis yield good result in terms of separation power and also validation accuracy when merging the LIBS and Raman data set. Metzinger *et al.* [15] used three comparative functions (linear correlation, sum of squared deviations, and overlapping integral), multivariate curve resolution-alternating least squares (MCR-ALS) combined with classification tree and discriminant analysis (DA) to provide discrimination for paper and print types based on LIBS spectra. 100% discriminate accuracy was achieved for paper but difficult for inks. The best result obtained by the novel MCR-ALS/DA approach for paper proved to be 96.3 % and 83.3 % accurate in the identification of print types.

The significance of the current study is to offer a more systematic study with the use of in-house matrix LIBS for elemental analysis of different kinds of black printing ink and to verify the reliability of this analytical tool with PCA.

MATERIALS AND INSTRUMENTATION

Materials

Throughout the study, standard 70 gsm white A4 papers from a manufacturer were used. Three identical square boxes (0.25 cm x 0.13 cm each) filled with genuine black ink were printed on the A4 paper. This step was repeated by different brands of inkjets, laserjets and photocopiers. The three square boxes were cut out from the paper sheet and placed on an XY translation stage that allows movement of the sample to a fresh location for each analysis. For control sample, the blank paper was processed like others sample but without printed ink on it. The combination of the control sample and printing ink samples resulted in a total of 10 samples, which were identified as shown in Table 1.

TABLE 1. List of types of printing ink with sample ID.

Types of printing machines/Control sample	Company/Model	Sample ID
Inkjet Printer	Brother/ DCP-5100	I1
	Canon/ E400	I2
	HP/ Desktop Ink advantage 2125	I3
Laser Printer	Canon/ Image class LBP701BC	L1
	HP/ LP1025 color	L2
	Fuji Xerox/ Docu Print CP225w	L3
Photocopier	Canon/ IR5055	P1
	Ricoh/Aficio 1060	P2
	Fuji Xerox/ Docucentre-IVC2263	P3
Control Sample (paper)	IK Yellow 70 gsm	Paper

Instrumentation

Current research used an in-house LIBS that equipped with a 1064 nm Q-switched Nd: YAG laser (MYCHWAY), lenses, UV-VIS optic fibre, spectrometer (Ocean Optics HR4000) and computer as output. The Nd: YAG laser has maximum single pulse energy that can reach 270 mJ with a pulse duration of 10 ns. The laser voltage is set as 900 mJ and integration time of 100 ms. A pair of lenses with focal length of 5 cm and 10 cm respectively was used to direct and collimate the laser beam. The collimated laser beam was further focused by another pair of lenses to allow ablation happened on the surface of the sample. The distance between the focusing lens and the sample is 5.2cm. A UV-VIS optic fibre with a core diameter of 60 μm was used to collect the emission from the plasma while the other end was connected to the entrance slit of the spectrometer. The LIBS was supported by the SpectraSuite (Version 10.1) software for record and visualise the spectra. The experiment took place in the ambient air.

Wavelength Calibration

Calibration remains as the crucial step in characterization technique. The calibration of spectrometer set up includes a “pencil-style” spectral lamp and the detection system Ocean Optics HR4000 used in the LIBS. The spectral lamp can provide distinct and well-defined lines at a known wavelength range. In this research work, the mercury lamp (Hg) and zinc lamp (Zn) (brand Philips) are selected to calibrate the spectrometer due to their good and specific respond in the range of visible and UV wavelength. The lamp illuminates the spectrometer, and the wavelengths of the calibration lines were recorded. The Spectra Suite software is used to analyse the result and compared with NIST Atomic Spectra Database. The difference between the wavelength from NIST and HR4000 of the same element had been calculated and averaged. Figures below presented the calibration wavelength spectrum for mercury (Figure 1) and zinc (Figure 2).

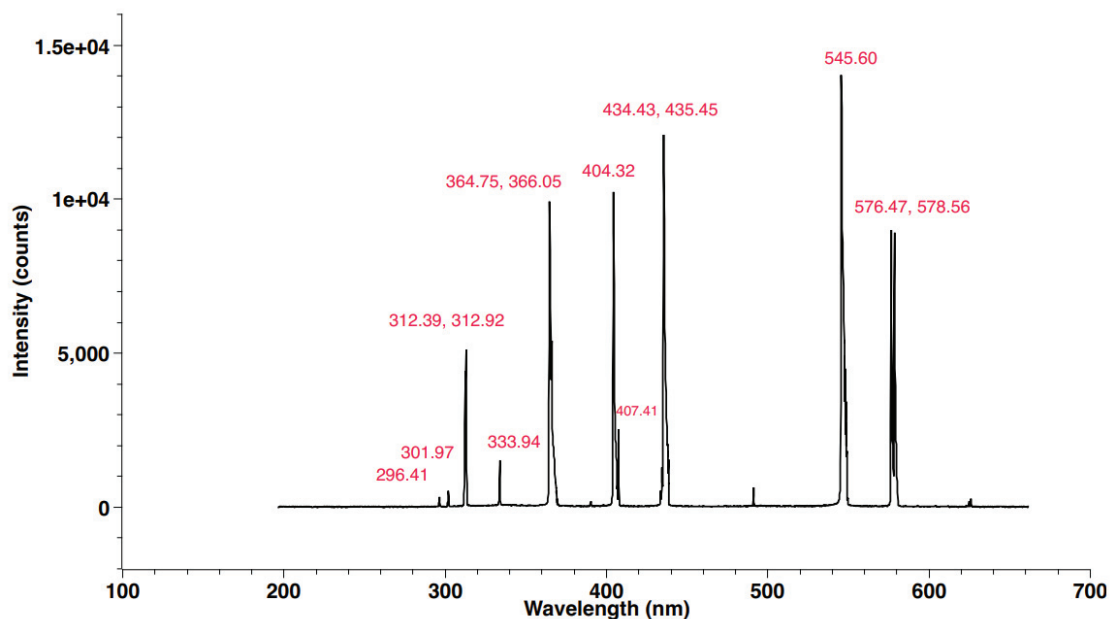


FIGURE 1. The calibration wavelength spectrum for mercury.

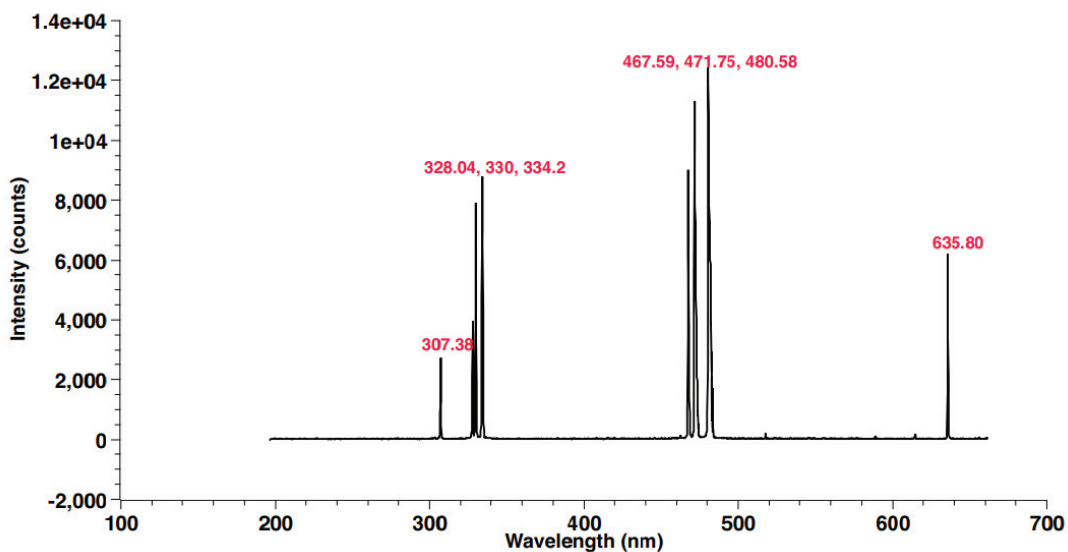


FIGURE 2. The calibration wavelength spectrum for zinc.

The total average difference for Hg lamp between the NIST atomic spectra database and HR 4000 is 0.32 nm. The spectrum had shifted to the left with an average value of 0.32 nm while for Zinc spectrum the average difference is 0.35 nm. The total average difference for the two elements lamp is accounted of 0.34 nm. However, it was noticed that the shifting was not linear. The shifting is in the range of 0.18 nm to 0.51 nm to the left.

RESULTS AND DISCUSSIONS

Identification of LIBS Spectral

Emission spectra for the paper and samples were recorded under optimised conditions of the LIBS technique. 200 LIBS spectra were collected from each sample and its replicates. Each spectrum was accounted to a fresh spot in the sample. The approach for the element identification consisted of the following steps: (1) Normalised the spectra between replicates, (2) split the spectrum into smaller relevant region of interests to do spectra overlay, (3) identify the elements of interests based on NIST atomic spectra database with a peak toleration of 0.12 nm to 0.51 nm as mentioned in section 2.2.1. The identification of the emission peak also takes into the accounts of the wavelength of the peak located (confirmed by two different persistent lines), follows by the intensity/transition probabilities of the element compare with NIST database and also the most possible elements that exist in the sample. For example, there are two peaks which corresponded to the excited neutral sodium (Na). The peaks are located at 588.57 nm and 589.18 nm. The spectra of the samples show that Na I (588.57 nm) has a higher intensity than Na I (589.18 nm). This characteristic is in agreement with the intensity provided by NIST atomic spectra database and also experiment done by Beldjilalii *et al.* [17] as presented in Figure 3. Figure 4 depicts the spectrum obtained for this research work.

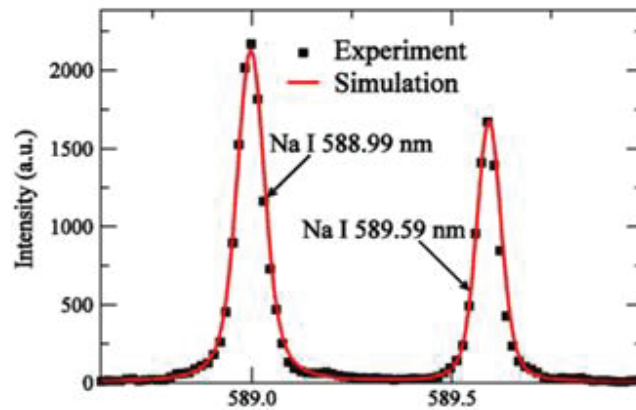


FIGURE 3. Experiment spectra of Na I recorded by Beldjilalii *et al.* [17].

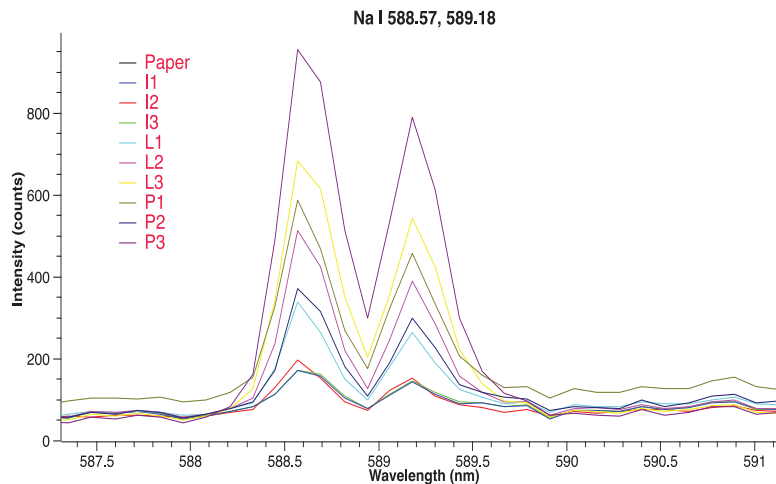


FIGURE 4. Experiment spectra of Na I observed among the samples.

The same process is repeated for other identified elements. The overall identified spectrum is presented in Figure 5 with the spectrum from paper and also sample P1 as an example.

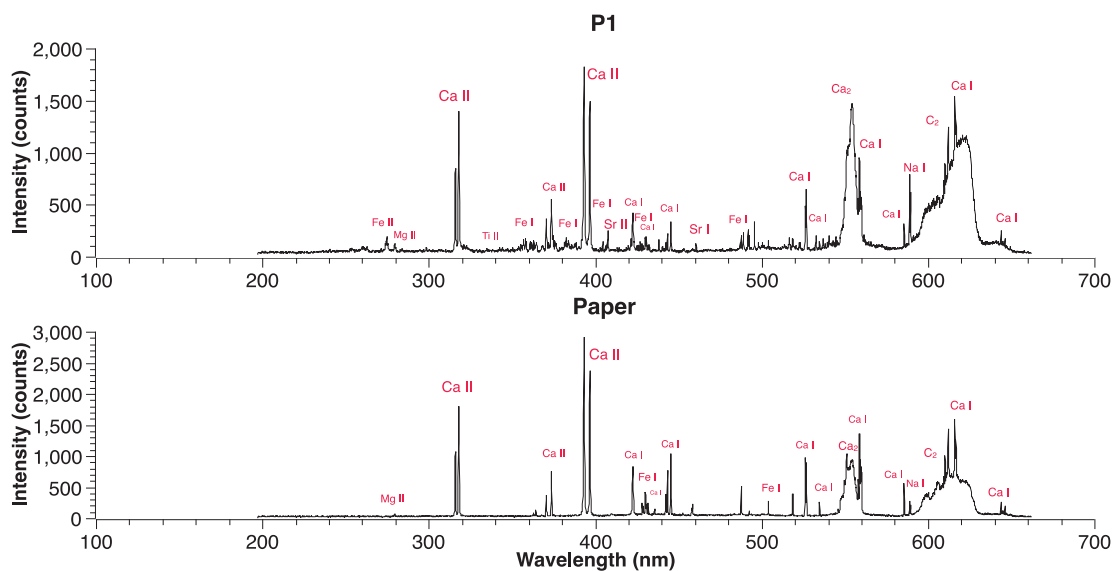


FIGURE 5. Overall spectrum for paper and sample P1.

The paper spectrum obtained from LIBS experiment consists of calcium, iron, magnesium and sodium. The elements are either in the form of neutral (I) or singly charged ions (II). The identified elements were supported by the research done by Kula et. al. [11], except present study, did not detect the presence of titanium (Ti) and silicon (Si). The detected elements are commonly found in the chemical used in paper manufacturing to increase the paper strength and resistance to water. As an example, the element calcium that detected by the LIBS may come from the most common fillers used in papermaking which is the ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC) [18]. The filler can smooth the surface of the paper and also improve the optical properties of paper such as opacity, brightness and colour. Emissions of diatomic species Ca_2 and C_2 were also observed in the region of 545-558 nm and 592-613 nm for all samples. Collisions in the plasma formed the diatomic species.

To minimise the effect of the paper spectrum on the printing ink analysis, only region 220-278 nm, 320-360 nm, 400-420 nm and 460-500 nm are selected for searching the lines derived from ink components. For example, Fe II and Mg II were detected in the region of 220-280 nm as shown in Figure 6. In the region of 220 to 278 nm, where element Fe II resided, paper substrate contribution was at the minimum. Meanwhile, for Mg II, the paper substrate contribution is as par of the printing ink samples.

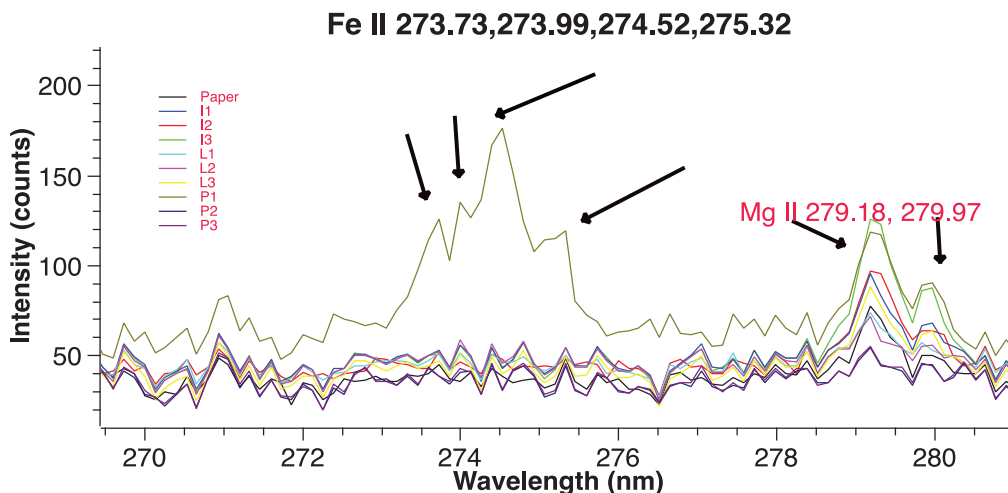


FIGURE 6. LIBS spectrum of the printing ink samples and paper in the region of 270 nm to 284 nm.

Among the printing ink sample, only quantitative differences between the elements were detected except for sample P1 which has a significant qualitative difference. The element strontium (Sr) was detected at wavelength 407.41 (II), 460.73 (I), and 421.27 (II). The peaks were unique compared to other samples. The spectrum were shown in Figures 7 and 8. Table 2 summarised the elemental profiles of the inks under investigation (Table 1) with minimum paper substrate obtained from LIBS analysis.

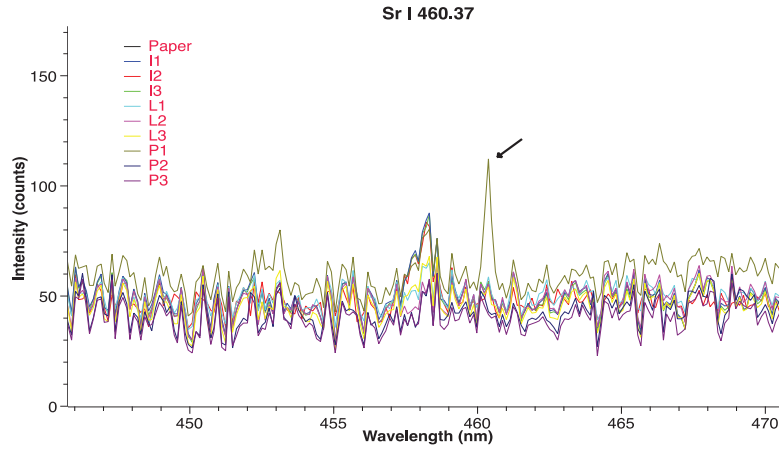


FIGURE 7. The peak of Sr I in the region of 445 nm to 470 nm.

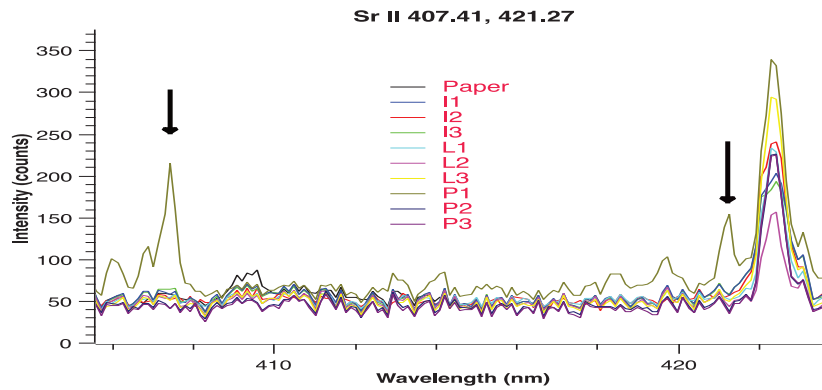


FIGURE 8. The peak of Sr I in the region of 445 nm to 470 nm.

TABLE 2. List of the elements detected by the LIBS with minimum paper substrate for printing ink analysis.

Index No.	Elements (Wavelength, nm)
1	Fe II 273.73
2	Fe II 273.99
3	Fe II 274.52
4	Fe II 275.32
5	Sr I 460.57
6	Sr II 407.41
7	Sr II 421.27
8	Ti II 334.60
9	Ti II 335.77

Comparative Study with PCA

The ability to discriminate between the alleged object and reference sample remains as critical part of forensic science. In this session, the principle analysis component (PCA) is used to evaluate the discrimination power of LIBS technique for the ten samples including paper based on their types of printing ink (viz. inkjet printer, laser printer, and photocopiers). The PCA was applied to the samples including paper using the MINITAB Version 17.1 statistical software (Minitab Incorporated, State College, PA, USA). All of the identified elements (Ca, Fe, Mg, Na Ti, and Sr) including those in the control sample and printing ink samples were subjected to the analysis. The outcome (in the form of score plot) will be those with similar scores are positioned closely together while those with different characteristic are away from each other. Interpretation is achieved using the first three PCs (PC1, PC2 and PC3). The total variation for the three PCs is 95.4% with 50% for PC1, 34.5% for PC2 and 10.2% for PC3. As score plot is two dimensional, a 3D scattered plot is done to visualise the 3 PCs.

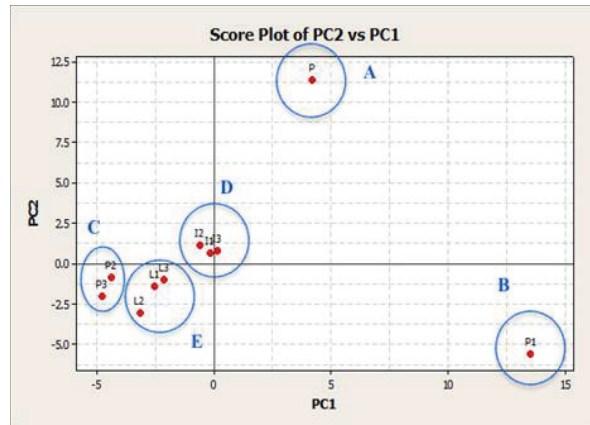


FIGURE 9. The score plot for the printing ink samples and control sample with manually drawn circle for differentiation between the cluster.

The score plot is capable of visualising the relationship between the samples. The samples were differentiated into 5 cluster group. Sample paper (P) was far away from other printing ink samples. The photocopiers, LaserJet, and inkjet printer samples were individually clustered among themselves. Only sample P1, which belongs to the photocopier group was away from the cluster zone C. The PC analysis can provide good separation between types of printing ink samples and also paper.

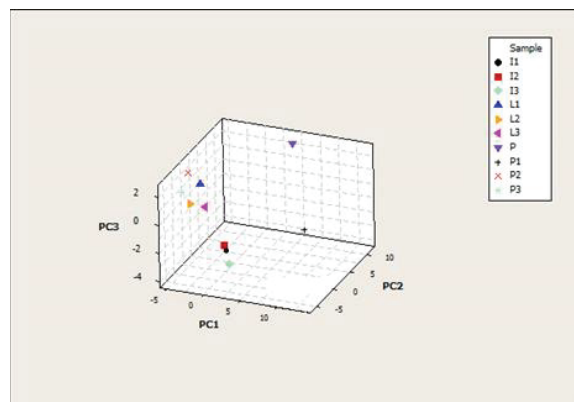


FIGURE 10. The 3D scatter plot for printing ink samples and paper.

In the 3D region, the sample from inkjet printers formed an independent group from other samples while paper (P) and sample P1 are away from the group. The samples from photocopiers (except P1) and also LaserJet printers were clustering in the zone near PC3 away from other samples.

CONCLUSION

LIBS analysis is compatible to be used as an analytical examination of printing ink from different types of printing mechanism. The elemental composition of black printing ink for photocopiers, LaserJet printers, and inkjet printers are established under optimised in-house matrix LIBS. Only sample P1 has qualitative differences compares to other samples. A further quantitative analysis can be done to provide more useful information.

The advantages of the laser-based analytical method include surface analysis, micro-destructive, analysis with minimum sample destruction, cost and time effective. The evaluation of discrimination capabilities of LIBS analysis with PCA proved to be fruitful with variation of 95.4 %. The LIBS analysis with PCA can separate the types of printing ink based on their printing mechanism.

In conclusion, LIBS can be a good alternative to standard chemical methods for examination of ink. Furthermore, the LIBS analysis provides inorganic profile of printing ink which is difficult to differentiate and detect by conventional methods.

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REFERENCES

1. R. D. Warner and D. R. M. Adams, *Introduction to Security Printing* (Graphic Arts Center Publishing Company, 2005).
2. K. A. Kennedy, *An Analysis of Fraud: Causes, Prevention and Notable Cases* (University of New Hampshire, Durham, 2012).
3. STM E1422-01, *Standard Guide for Test Methods for Forensic Writing Ink Comparison* (ASTM International, West Conshohocken, 2001).
4. S. Ahmed, *Technology of Printing Inks* (Jamia Milia Islamia, New Delhi, 2007).
5. H. Mollet and A. Grubenmann, *Formulation technology: emulsions, suspensions, solid forms* (John Wiley & Sons, Weinheim, 2008).
6. J. Brader and I. Thorn, *Surface Application of Paper Chemicals* (Blackie Academic & Professional, London, 1997).
7. V. Causin, *Polymers on the Crime Scene: Forensic Analysis of Polymeric Trace Evidence* (Springer International Publishing Switzerland, Cham, 2015).
8. K. janssens, G. Vittiglio, I. Deraedt, A. Aerts, B. Vekemans, L. Vincze, F. Wei., I. De Ryck, O. Schalm, F. Adams and A. Rindby, *X-Ray Spectrometry* **29**(1), 73-91 (2000).
9. A. Koenig, *Laser* **24**(88Sr), 12C (2003).
10. A.-M. Olsson, T. Calligaro, S. Colinart, J. Dran, N. Lövestam, B. Moignard, and J. Salomon, *Nucl. Instrum. Meth. B* **181**, 707-714 (2001).
11. A. Kula, R. Wietecha-Posłuszny, K. Pasionek, M. Król, M. Woźniakiewicz, and P. Kościelniak, *Sci. Justice* **54**, 118-125 (2014).
12. T. Trejos, A. Flores, and J.R. Almirall, *Spectrochim. Acta B* **65**, 884-895 (2010).
13. C. Lennard, M.M. El-Defdar, and J. Robertson, *Forensic Sci. Int* **254**, 68-79 (2015).
14. R. Corzo, K. Subedi, T. Trejos, and J.R. Almirall, *J. Forensic Sci* **61**, 725-734 (2016).
15. A. Metzinger, R. Rajkó, and G. Galbács, *Spectrochim. Acta B* **94-95**, 48-57 (2014).
16. M. Hoehse, A. Paul, I. Gornushkin, and U. Panne, *Anal. Bioanal. Chem* **402**(4), 1443-1450 (2011).
17. S. Beldjilali, W.L. Yip, J. Hermann, T. Baba-Hamed, and A. Belasri, *Anal. Bioanal. Chem* **400**(7), 2173-2183 (2011).
18. J.Grönfors, "Use of fillers in paper and paperboard grades," Final thesis, Tampere University of Applied Sciences, 2001.