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Elemental Analysis of Printing Ink with the Application of Laser-Induced Breakdown Spectroscopy (LIBS)- A Review

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ABSTRACT

Forgery cases involving printed documents have recently increased due to advanced printing technologies. As a result, various analytical instruments are currently applied in forensic document examination to analyse printing ink. Analyses of printing ink are primarily focused on the ink's chemical components, namely colourants, vehicles, and additives. Previous studies on ink analysis show an increasing trend in the use of spectroscopy methods including the application of Laser-Induced Breakdown Spectroscopy (LIBS). This instrument is favoured by document examiners in analysing printing ink due to its versatility, simple preparation, multi-elemental detection, minimal destruction, and precise readings. The examination of printing ink using LIBS is reviewed in this publication in addition to findings from previous research. The strengths and drawbacks of this technique, as well as contemporary approaches, are also explored in this article.

1. Introduction

The growing market and demand for advanced printers, computers, scanners, and photocopiers have fuelled the progress of printing technology. This progress has increased the forgeries of documents in printed form, such as academic certificates, currency, medical records, insurance papers, wills, contracts as well as travel and identity documents [1-8]. Therefore, ink analysis of printed documents has become indispensable in verifying questioned documents. Questioned documents refer to any form of written or printed texts on various substrates (paper, banknotes, etc.) with questionable authenticity and these documents can be treated as evidence in civil or criminal cases [9]. The first analysis of printing ink in 1914 was performed to determine ink composition and detect harmful materials [10]. High-speed computer printers were invented in 1953 causing a large influx of printers for personal or commercial uses [11-16]. As a result, the trend of ink

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analysis from printing inks took off in the 1960s [11-16]. Printing technology nowadays has advanced to three-dimensional (3D) printers, which offer numerous advantages for various industries [17,18].

Generally, printed documents can be categorised based on their ink type namely toner, inkjet, offset, and intaglio. Printing ink contains vehicles (resin and/or solvent) with flowing or drying characteristics that dissolve or suspend the colourants [8,19-21]. The colourants in printing ink may be pigments (e.g., carbon black, phthalocyanines) [20-23] or dyes (e.g., Congo red, Methylene blue, crystal violet) [24,25]. Inorganic and organic additives are added to the mixture contributing specific properties, modifying the drying process, influencing the ink's actual appearance, or controlling the density or flowing characteristic of the ink [21,26]. As a result, a wide variety of substances, according to the ink's type, brand, and batch, provide unique chemical signatures which are beneficial to forensic scientists [3,27]. Although the exact chemical composition of a particular ink is undisclosed by its manufacturers, each ink variant has a unique fingerprint in terms of its analytical makeup.

A Forensic Document Examiner (FDE) plays a role to ascertain the authenticity of documents by detecting alterations, deletions, and obliterations as well as establishing the exact point in the document's printing time. Thus, FDE is encouraged to apply analytical techniques to provide a highly-accurate ink analysis. Previous studies on printing ink depended on chemical or elemental compositions of ink, intersecting printing lines, ink dating, paper analysis, etc. FDE commonly employs visual examinations such as microscopic analysis and light examination with Visual Spectral Comparator (VSC) [6,28,29]. However, these techniques are subjected to human error and the results are inadequate to investigate the authenticity of the documents [28,29]. Hence, it is necessary to apply further chemical analysis for improved characterisation and discrimination of the ink.

Numerous analytical approaches (destructive and non-destructive) have their purposes in printing ink analysis as reported in the scientific literature [26]. Destructive techniques are time-consuming with delicate sample preparation, which eventually damages the samples. Despite their destructive nature, these techniques are still practised in forensic analysis due to their powerful compound identification in ink [3,14,27-34]. Some examples of destructive techniques are mass spectrometry, capillary electrophoresis, and High-Performance Thin Layer Chromatography (HPTLC). In contrast, non-destructive techniques require minimal sample preparation with the added advantages of multiple measurements and preservation of the documents' integrity [4]. These techniques involve utilising spectroscopy instruments that are occasionally used in tandem and conjunction with multivariate data analysis. Infrared (IR), Raman, and elemental spectroscopy are a few examples of non-destructive techniques [4,31,35-43].

Laser-Induced Breakdown Spectroscopy (LIBS) is an atomic emission spectroscopy that applies the use of laser ablation. LIBS is first applied by Brech and Crossin [44] and along the way, LIBS has found its way into other fields of study, such as biology [45-49], geology [50], astronomy [51], archaeology [52-55], and artistic prints [53,58-60]. LIBS is a semi-destructive elemental analysis that employs a surface technique using laser ablation with high sample throughput [8,61-63]. This cost-effective instrument collects information from the ablated mass with high sensitivity and precision [6,8,61,62]. To date, only seven studies on the application of LIBS in printing ink analysis exist due to the infancy of LIBS in this area of forensic interest. Therefore, this paper discusses the pros and cons of LIBS in printing ink analysis by reviewing the results from previous research to determine the aptness of this technique for printing ink. The hybrid of LIBS with other instruments and its role in multivariate data analysis are also discussed.

2. LIBS' Principles

LIBS is considered a relatively recent innovation in forensic science thus, its features such as lasers, spectrometers, and detectors are constantly being upgraded [61]. LIBS is compartmentalised into several subsystems; a pulsed laser focused by lenses on the target, a delay pulse generator, an ablation cell for the plasma formation, an optical system to collect emitted signal, a spectrometer with a sensitive detector, and a computer [8,63-66]. Besides the type of laser, the configurations of the spectrometer-detector and time control unit, environmental factors should be considered to improve any experiment with LIBS [67]. Figure 1 shows a typical setup for LIBS.

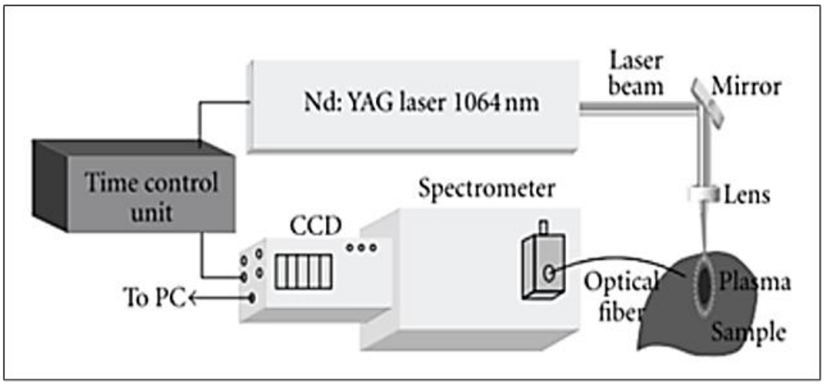

Fig. 1. Typical setup of LIBS [67]

A highly energetic laser-pulsed beam (in nanosecond ranges) is aimed at the sample surface to provoke optical sample excitation and induce the plasma [3,64,67,68]. Consequently, this light energy causes the ablation of a small sample mass and the creation of high-temperature plasma. The temperature of the sample surface rapidly increases up to the vapourisation threshold [65,67]. This process causes phase change at the sample surface and several other phenomena, such as photoelectron emission and plasma formation [65]. The parameters of laser-produced plasma are determined by the excitation temperature and electron density [69]. The plasma with excited atoms and ions of the analysed sample produces discrete lines, bands, and an overlying continuum [3,65-67]. The discrete lines consist of intensity, shape, and wavelength which help characterise the samples [3,67]. The laser energy directly affects plasma emission spectra and the signal-to-noise ratio [70].

Besides laser energy, the laser wavelength is crucial in the formation of plasma [69]. The suitable wavelength is selected depending on the expected analytical work with LIBS [69]. Besides that, the time delay parameter in LIBS is as important as the laser energy due to the dynamic processes of plasma formation and radiation [70]. The time delay allows the decay of the continuum radiation before the spectral measurements [66,70]. The spectra are affected by time variation in which the dissipation of the laser plasma and the formation of the spectrum occurs in microseconds [66]. The process of selecting time delay (gate delay) and integration time (gate window) must be based on the laser wavelength, which subsequently affects the signal-to-background ratio [67]. An optimised delay can minimise interferences and improve signal intensity however, a longer time delay can cause lower signal intensities [62,70].

The plasma emission is directed to a spectrometer (e.g., Czerny-Turner and Echelle) with optical fibres and/or lenses [58,61]. The spectrometer is used to diffract the collected light, which then is dispersed by a grating, thereby producing "spectral signatures" of the sample [8,67,68]. Subsequently, a sensitive detector detects the light, such as a photomultiplier tube (PMT), a photodiode array (PDA), or a charge-coupled device (CCD) [8,67]. Finally, the computer connected to the system is used for data storage and processing of the acquired spectrum. The raw data (intensity versus wavelength) can be obtained from the spectrum with spectral lines that are formed based on elements present in the samples [61]. The spectral lines are typically shown in wavelengths ranging from 190 to 900 nm. The National Institute of Standards and Technology (NIST) database can be used for comparison of the wavelengths [8,16,61,71]. Additionally, simultaneous quantification is possible and the concentration of the elements can be determined based on their emission intensity [8].

2.1 Stages of Plasma Lifetime in LIBS

Optimising the parameters for LIBS measurements requires an understanding of LIBS' plasma physics [67]. Consideration of the environmental factors that may affect the plasma lifetime and features is also necessary [67]. The plasma lifetime is divided into three stages, as seen in Figure 2 below [67]. Several processes occur as the laser evokes the creation of plasma. It begins with the emission of continuous Bremsstrahlung [65,69]. Plasma ignition is the first stage of plasma lifetime occurring during the laser pulse which breaks the bond and shields the plasma. The interaction of laser and matter causes the absorption of photons by atoms. This absorption causes the electrons to acquire higher energy levels [67]. This process is affected by the duration of the laser pulse, irradiance, and laser type. The plasma becomes opaque for the last leg of laser radiation during the plasma shielding effect. At this stage, the laser pulse is either reflected or absorbed by the plasma surface. The radiation does not reach the sample surface which prevents the ionisation of the material and reduces the ablation rate. Then, the craters are formed with melted and deposited material around them. Simultaneously, the size and lifetime of the plasma are multiplied when the plasma is reheated.

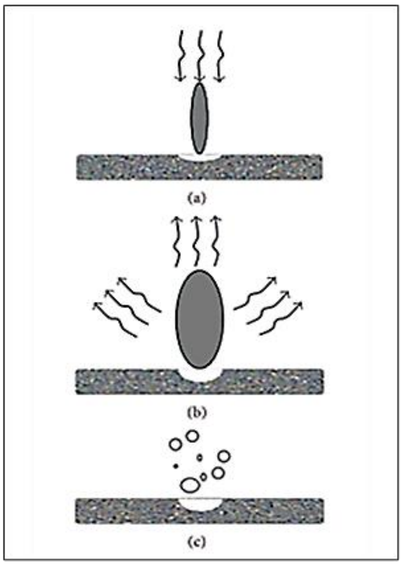

Fig. 2. Stages of plasma lifetime which are (a) ignition of plasma, (b) expansion and cooling of plasma, and (c) ejection of particle and condensation [67]

The following stage is the expansion and cooling of the plasma. The factors that influence this stage are spot size, environmental aspects, ablated mass, and energy coupled to the plasma [67]. Atomic emission occurs during the cooling process thus, this stage is vital to optimising the acquisition of LIBS spectra. Moreover, recombining electrons and ions in this stage is compulsory to give rise to line emission, which influences the radiation processes [69]. After the ignition process, plasma expansion, and cooling continue meanwhile, electron temperature and density change simultaneously. As the electrons downshift to lower energy levels, the electrons emit photons in the decay. This process is synonymous with the de-excitation of atoms [67].

Line emissions are more visible after plasma formation as the plasma cools down. However, line emissions are hidden in the continuous emission due to radiative recombination and the Bremsstrahlung effect [65,67]. The plasma radiation first appears as a continuous spectrum that fades quickly in the wake of plasma relaxation [65,69]. This radiation constitutes atomic lines from decays of excited atoms, ions, and small molecules [65,69]. The distinct energy levels of different atoms cause them to emit characteristic photon energies with narrowband emissions forming the spectral emission lines in LIBS spectra. Therefore, a time delay in the time control unit is required to avoid the continuum radiation [65,67]. The final stage of the plasma lifetime is particle ejection and condensation which are insignificant for LIBS measurements [67]. A portion of the materials is ablated as particles that cause the exfoliation of a solid sample, formation of condensed vapour, and ejection of a liquid sample.

3. Instrumental Setup of LIBS in Previous Studies

The setup of LIBS involves selecting the best laser source as the light energy and the configuration of laser parameters such as wavelength, pulse time, and laser energy. Optimisation and calibration of LIBS parameters are imperative to acquire the highest intensity of signals without saturating the spectrum [2,62]. Due to the resultant craters after laser ablation, the size of the craters should be considered to ensure the least amount of ablated substrate on which the ink was printed. Previous research's instrumental setup and parameters of LIBS for printing ink analysis are summarised in Table 1.

As seen in Table 1, the most common laser used in previous studies was Nd:YAG [1,2,7,62,68,73]. This laser type with a fundamental wavelength of 1064 nm is the preferred light source in LIBS as it can quickly generate compact plasma [67]. As highlighted by Anabitarte *et al.,* [67], a higher laser wavelength produces a lower ablation rate with a higher elemental fractionation. A study by Metzinger *et al.,* [72] used a different laser type (Nd:GGG) due to a change in the LIBS system. The intensities of LIBS signal emission were increased by configuring the emission of laser pulses (Table 1). Several authors used Czerny-Turner [62,68] and Ocean Optics [1,2] spectrometers in their studies. Czerny-Turner spectrometer is common in LIBS which consists of a diffraction grating, an entrance slit, and two mirrors [67]. The slit is passed through with the light which hits the first mirror. The mirror pivots the light onto the diffraction grating before the light is directed onto the focal plane with the detector by the second mirror.

The application of the instrument determines the suitable detectors to be used. CCD was equipped by several authors as the detector for printing ink analysis [7,62,72,73], while the rest did not divulge details on the type of detector [1,2,68]. CCD detectors provide less background signal for two-dimensional spatial information [67]. As for ablation spot size, several authors measured its size, and they observed spot size on paper samples (200 – 300 µm) was smaller compared to banknote papers (0.6 – 1.0 mm) [1,7,73]. Subedi *et al.,* [73] explored the use of a tandem system of LIBS with LA-ICP-MS. As explained by the authors, sample excitation by the emitted light is collected by a fibre optic in the LIBS plasma to a CCD spectrometer. The ablated particles were transported by an argon carrier to the inductively coupled plasma (ICP). The laser energy was varied by the authors according to the types of ink in which inkjet ink consumed the highest energy (13 mJ). Additionally, laser frequency was varied according to ink type. A higher frequency was used for toner ink (1.8 Hz), offset ink (4 Hz), and intaglio ink (4 Hz) compared to inkjet ink (0.8 Hz) [73]. High frequency can cause more damage to the samples. Therefore, low frequency is more suitable for inkjet ink to minimise interferences from paper since this ink type is immersed in the paper.

Table 1
List of the instrumental setup of LIBS in previous studies

Type of sample	Laser source (wavelength; energy; type)	Spectrometer	Time delay	Detector	Spot size	Additional notes	Ref.
Ink on paper	1064 nm; 170 mJ; Nd:YAG	Ocean Optics LIBS2500+ spectrometer	2.6 µs	Not available	300 µm	The sample chamber was purged with argon gas for 60 s for air removal and increased spectral intensity. The analysis mode was line mode.	[1]
Ink on paper	1064 nm; 270 mJ (10 ns); Nd:YAG	Ocean Optics HR4000 spectrometer	Not available	Not available	Not available	The research was performed in ambient air using 60 µm UV-Vis optic fibre. Integration time was fixed at 100 ms for a laser voltage of 900 mJ.	[2]
Ink on paper	1064 nm; Not available; Nd:YAG	6-channel broadband spectrograph (190 – 1040 nm)	1.4 µs (inkjet) & 1.2 µs (toner)	CCD linear array	300 µm	35% energy was used for 150 shots with a 25 µm/s speed rate at a 2 Hz frequency and 1.1 ms of integration time.	[7]
Ink on banknote papers	1064 nm (spectra collected at 185 – 904 nm UV-Vis ranges); 150 mJ; Nd:YAG	6-channel Czerny-Turner	Not available	CCD	0.6 to 1 mm	The experiment was performed at atmospheric pressure by running the laser for 6s. The spectral resolution was around 0.1 nm.	[62]
Ink on pharmaceutical packages	266 nm; 5.4 mJ; Nd:YAG	6-channel Czerny-Turner (190 – 1040 nm ranges)	0.9 µs	Not available	100 µm	The ablation mode used a straight-line mode.	[68]
Ink on paper	198 – 318 & 345 – 888 nm (UV & Vis ranges, respectively); 10 mJ; Nd:GGG	Two-channel fibre optic spectrometer	40 µs (double-pulse mode)	CCD	Not available	A micro-LIBS system was used with two consecutive laser pulses that have similar energies with an integration time fixed at 2 ms. The measurements were performed under argon gas.	[72]
Ink on paper	1064 nm; 4.1 mJ (offset & intaglio inks), 13 mJ (toner), 7.8 mJ (inkjet); Nd:YAG	6-channel broadband spectrometer	0.1 µs (inkjet, offset & intaglio) & 0.8 µs (toner)	CCD linear array	200 µm	Laser Ablation – Laser Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) was used in tandem with LIBS. The ablation mode was single-line mode.	[73]

4. Elemental Analysis of Printing Ink

LIBS is a compact and stand-alone system that is capable of simultaneous rapid multi-elemental detection and surface analysis (<1 second per analysis) [7,62-64,66,74]. This instrument can analyse any material in various physical states i.e., solids, liquids, gas etc. [66,70,74]. There is no requirement to prepare or treat the sample before analysis. This non-existent prerequisite preserves the sample integrity, which is favourable for ink samples [3,66]. LIBS can perform atomic-level quantitative and qualitative chemical analyses by properly identifying a specific element (in an ionised or neutral state) for each emission line [67]. Moreover, pre-set elemental menu is not necessary for LIBS, unlike in LA-ICP-MS. Broadband scanning can be performed using LIBS and it is useful for the detection of unusual peaks [7,73]. In printing ink analysis, LIBS can provide inorganic information about the ink. This feature is a rarity in standard techniques [72]. Qualitative analysis can be carried out accurately as it detects the atomic emission of all elements in the analysed sample [67].

Quantitative analysis of LIBS determines the relative number of elements in units of ppm (concentration of elements), ng (absolute mass of elements), or ng/cm^2 (surface concentration) [67]. This analysis encompasses the non-calibration method and calibration method. The latter uses a calibration curve tied to experimental factors [67,75]. However, the optimisation and development of LIBS are time-consuming [1]. Furthermore, LIBS may not be sensitive enough in the quantitative analysis compared to other atomic emission spectroscopies [66]. Additionally, spectral noise can interfere with elemental analysis which can be caused by the presence or absence of distinct emission lines [56]. Nonetheless, generating reproducible spectra that show consistent qualitative differences through a selection of valid spectral lines can provide a solution to this problem [62].

Another difficulty of using LIBS is interpreting multivariable data in large amounts within a short period [2,61]. A reliable overall data analysis could not be achieved when interpreting an abundance of spectral lines. However, multivariate data analysis can be applied for a systematic classification and differentiation of the samples. LIBS is also a semi-destructive instrument, leaving a small visible crater after the laser ablation [2,3,6,63]. Metzinger *et al.,* [72] microscopically scrutinised the images of before and after LIBS measurements on inkjet and toner ink on paper. They observed that the diameter of all craters after ablation was tenfold or a hundredfold bigger in size compared to the size of all prints which was only a few µm in diameter. Deep craters were observed on inkjet ink with 30 µm to 95 µm in diameter. The low density of the fibrous structure of the paper causes higher penetration of laser on inkjet ink. For toner ink, the ablation only affected the toner layer since the light energy is highly absorbed in the layer. The toner particles had a weak adhesion to the paper fibre, and their heat conduction was higher than the materials in the paper. Despite these disadvantages, several authors argued that LIBS is a viable technique to distinguish printing ink from various sources [2,7].

4.1 Detected Elements in Previous Studies

The elemental composition of printing ink can vary due to the mixture of chemical components created during the manufacturing process [7]. Instead of a complete quantitative method, qualitative and semi-quantitative data from intensities of the peak are favoured for samples of toner and inkjet ink. The detected elements in previous studies are listed in Table 2. Most studies provide detailed information on types of ink, except the research conducted by Hui *et al.,* [2]. The most analysed ink types are toner and inkjet ink printed on paper as substrate [1,2,7,72,73]. Only two studies analysed printing ink on banknote papers [62] and pharmaceutical packages [68].

Table 2
List of elements found in printing ink

Sample	Elements														Ref.
	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hf	I	K	Mg	Mn	Na	
Toner and inkjet ink on paper	×	×	×	×	×	×	×	/	×	×	×	×	×	×	[2]
Toner ink on paper	×	×	/	×	×	/	/	×	/	×	×	/	×	×	[1]
Toner ink on paper	/	×	×	×	/	×	/	/	×	/	/	/	/	/	[7]
Toner ink on paper	×	×	/	×	×	×	×	/	×	×	×	×	×	/	[72]
Toner ink on paper	×	×	/	×	×	×	×	/	×	×	/	×	/	/	[73]
Inkjet ink on paper	×	×	/	×	×	/	/	×	×	×	×	/	×	×	[1]
Inkjet ink on paper	×	×	×	×	/	×	/	×	×	×	/	/	×	×	[7]
Inkjet ink on paper	/	×	/	×	×	×	×	×	×	×	/	×	×	/	[73]
Offset ink on paper	/	/	/	×	/	×	/	×	×	×	/	/	/	/	[73]
Intaglio ink on paper	/	×	/	×	/	×	/	×	×	×	/	/	/	/	[73]
Ink on banknote papers	/	×	/	×	/	/	×	/	×	×	/	×	/	/	[62]
Ink on pharmaceutical packages	/	/	/	/	×	/	/	/	×	×	/	/	/	×	[68]

/ denotes the presence of the element in the sample
× denotes the absence of the element in the sample

Table 2 (continued)
List of elements found in printing ink

Sample	Elements															Ref.
	Nb	Ni	Pd	Rb	Rh	S	Sb	Sc	Si	Sr	Ti	V	Y	Zn	Zr	
Toner and inkjet ink on paper	×	×	×	×	×	×	×	×	×	/	/	×	×	×	×	[2]
Toner ink on paper	×	×	/	×	/	×	×	×	/	/	/	/	×	×	×	[1]
Toner ink on paper	×	/	×	/	×	/	/	/	/	/	/	/	/	/	/	[7]
Toner ink on paper	×	×	×	×	×	×	×	×	×	×	/	×	×	×	×	[72]
Toner ink on paper	×	×	×	×	×	×	×	×	/	×	×	×	×	×	×	[73]
Inkjet ink on paper	×	×	×	×	×	×	×	×	/	/	×	×	×	×	×	[1]
Inkjet ink on paper	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	[7]

Inkjet ink on paper	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	[73]
Offset ink on paper	×	×	×	×	×	×	×	×	/	/	/	×	×	×	×	[73]
Intaglio ink on paper	/	×	×	×	×	×	×	×	×	/	/	×	×	×	/	[73]
Ink on banknote papers	×	/	×	×	×	×	×	×	×	×	/	×	×	×	/	[62]
Ink on pharmaceutical packages	×	/	×	×	×	×	×	×	/	/	/	×	×	×	×	[68]

/ denotes the presence of the element in the sample
× denotes the absence of the element in the sample

Several authors employed the conventional technique of spectral overlay as the data acquisition approach [2,7,68,73]. According to Trejos *et al.,* [7], errors can be minimised using this approach when spectral regions with below detection limit and linear response are used for comparison. Two independent examiners reviewed the spectral data for similarities and differences of the replicated spectra to differentiate the samples [7,31]. Acquired spectra were first divided into smaller regions of interest. The signals between replicates for each region were normalised with background subtraction in LIBS software [2,7]. Elements beyond the detection limit were identified with peak search tolerance comparable to spectra resolution. This step marked the variability within the samples by comparing replicates of the samples. At least two spectral lines for each element were selected for visual comparison and confirmation [2,7,31]. The researchers then observed significant differences between the samples, such as spectral shapes and their relative peak heights. The samples were discriminated if any significant difference was detected [2,7].

As shown in Table 2, inkjet ink samples contain fewer elements compared to other types of ink [21,62,72]. Several authors identified similar elements in inkjet ink namely Ca, Mg, Cu, and K [1,7,73]. The element of Li was observed to be present in inkjet ink but this element was absent in other types of ink. Li plays a vital role in inkjet printing for electrical conductivity [7,73]. In addition, elements namely Al, Co, Sr, Si, Cr, and Na were discovered by several authors in inkjet ink [1,7,73]. Chemical formulations used in inkjet ink may cause fewer elements to be detected in this ink than in toner ink [73]. Furthermore, inkjet ink was partially absorbed in paper fibre. This absorption caused poor discrimination due to interferences from high paper contribution [72]. In contrast, toner ink was deposited onto the paper surface. Therefore, this ink type was discriminated efficiently [72].

A tandem LIBS-LA-ICP-MS discovered a similar observation in which inkjet ink was primarily embedded in the paper fibre while the layers of other types of ink (intaglio, offset, and toner ink) were slightly raised above the paper [73]. Lennard *et al.,* [1] selected emission lines for detected elements in toner ink samples namely Ca I (643.91 nm), Cr I (520.84 nm), Cu I (327.36 nm), Hf II (325.37 nm), Mg I (285.21 nm), Pd I (324.27 nm), Rh I (332.3 nm), Si I (288.21 nm), Sr II (460.73 nm), Ti I (498.17 nm), and V I (440.82 nm). As for Hui *et al.,* [2], only several spectra regions of interest (ranging from 220 nm to 500 nm) were used to detect emission lines from ink compositions to reduce the contribution from paper spectra. Figure 3 shows the peaks of Fe II and Mg II appearing in regions of 220 nm to 280 nm [2]. A minimal paper contribution was observed for Fe II, but the paper contribution was similar to the ink component for Mg II [2].

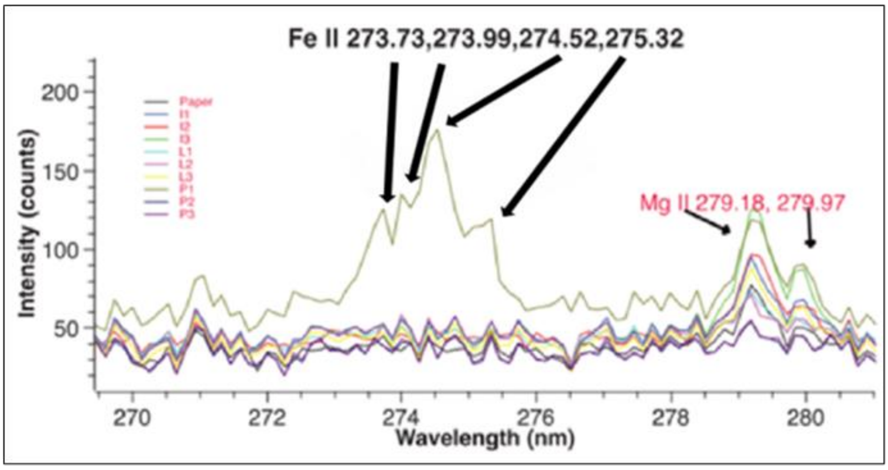

Fig. 3. Emission lines of elements Fe II and Mg II in samples with a paper contribution [2]

Moreover, only quantitative differences were observed for all toner ink samples except for one photocopier sample that showed qualitative differences [2]. This sample showed unique lines of Sr at wavelengths 407.41 nm, 460.73 nm, and 421.27 nm. Trejos *et al.,* [7] detected 20 elements in toner ink which was the highest number of elements compared to other studies. The authors detected I, Ni, Rb, Sb, Sc, S, V, and Y in toner ink samples that went undetected in other studies [7]. Meanwhile, only Lennard *et al.,* [1] detected Rh, Pd, and Hf. As reported by Metzinger *et al.,* [72], carbon-based particles or soot were commonly found in most black toner ink samples, but iron oxide was present in one of the samples. Fewer lines and lower intensity in the structured background were observed in UV spectra compared to Vis spectra as explained by the authors. Furthermore, the detection of Zr, Nb, and Hf in toner ink samples is expected since these elements had been included in several patents and books for toner ink formulations [76,77]. Subedi *et al.,* [73] analysed offset and intaglio inks. They postulated that each of these ink types had a single element that was absent in other ink. As for offset ink, Ba was detected where else Nb was discovered in intaglio inks only [73].

Król *et al.,* [62] proved the presence of Mn as the most frequent element in the banknote papers with the addition of other elements namely Al, Ca, Na, and Ti. Banknote papers contain the element of Ti due to the addition of titanium oxide during manufacturing. Authentic and counterfeit banknotes have different ratios of elemental profiles. Furthermore, the spectra of banknotes can be distinguished from standard office paper based on the number of lines in the spectra. The spectrum of banknotes showed more lines arising from singly charged ions, molecules, and neutral species compared to the office paper spectrum. Previous studies have proven that counterfeit banknotes are printed on standard office paper [62]. The spectral differences between banknotes and office paper are the basis to tell counterfeit banknotes apart from authentic banknotes. In addition, the authors studied the discrepancies between new banknotes and used banknotes. Qualitative differences can be observed in the spectra of both banknotes in several samples. Several used banknotes showed additional emission lines from Fe I at wavelengths from 371.965 nm to 374.942 nm, as shown in Figure 4. These peaks may arise from contamination due to contact with human skin and metallic parts of items, for instance, pockets, wallets, and purses.

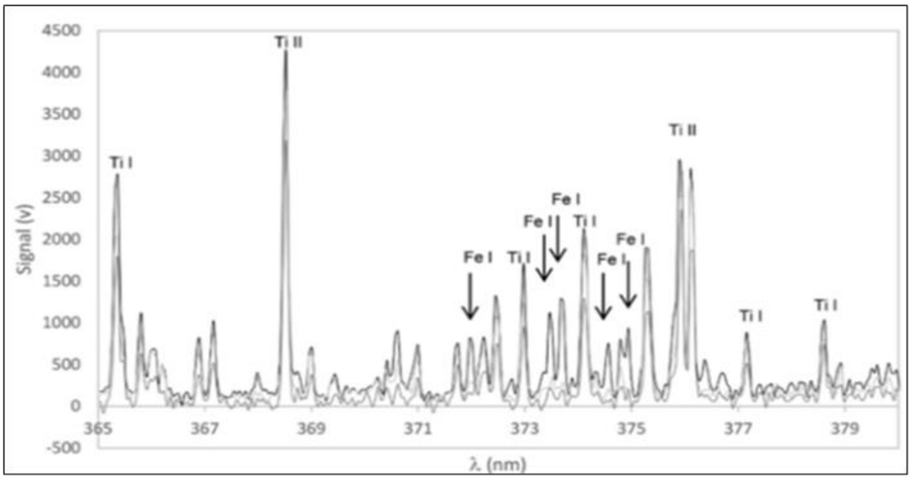

Fig. 4. LIBS spectrum of used banknotes with additional lines of Fe I as contamination [62]

Analysis of printing ink on pharmaceutical packages by Haase *et al.,* [62] discovered qualitative and quantitative differences between authentic and counterfeit packages. The authors described quantitative differences in signal intensities for peaks of Ca at 397 nm and K at 766 nm for the P1 sample (authentic package) and the C4 sample (counterfeit package). Samples P1 and C4 also showed qualitative differences with peaks of Mg (285 nm), Si (288 nm), and Al (396 nm). These elements were only found in the authentic package. As seen in Table 2, most of the detected elements (Al, Ca, Cr, Cu etc.) were similar to ink on paper except for Cd, which was detected on pharmaceutical packages only.

5. Comparison of LIBS with Other Spectroscopic Techniques

Several studies applied LIBS in conjunction with other spectroscopic instruments such as Attenuated Total Reflectance – Fourier Transform (ATR-FTIR) spectroscopy, Micro X-ray Fluorescence (µXRF) analysis, Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS), and LA-ICP-MS. Table 3 summarises the comparison of LIBS with these techniques for the analysis of printing ink.

Subedi *et al.,* [73] built a tandem LIBS-LA-ICP-MS for the analysis of toner, inkjet, intaglio, and offset ink (Table 3). This hybrid enhanced discrimination ability and diminished interferences. The results from this tandem system presented a thorough chemical composition of printing ink. The authors further explained that the optimisation was performed differently in standalone mode compared to tandem mode due to different principles of the techniques. In LIBS, the excitation of atoms and ions and the correct timing for emission line acquisition are crucial for optimisation. As for LA-ICP-MS, the critical factors are sub-micron-sized particles' production and efficient transport. The authors prioritised LIBS optimisation before adjusting the parameters to LA-ICP-MS for tandem mode. Consequently, some sensitivity of ICP-MS was withdrawn to encourage the improved performance of both methods.

Elemental information provided by tandem LIBS-LA-ICP-MS was complementary, which could not be obtained when these instruments were used individually. Additional elements were detected by LIBS that discriminated indistinguishable samples in LA-ICP-MS and LIBS observed fewer interferences with better signal-to-noise and reproducibility for Fe, Ca, K, and Si. Moreover, LIBS successfully detected certain elements (Si, Ca, and K) that are problematic as a result of isobaric interferences in LA-ICP-MS [7,73]. LIBS could not detect all elements due to its lower sensitivity, as opposed to LA-ICP-MS. This fact underscores the superiority of LA-ICP-MS over LIBS. Nevertheless, LIBS is an alternative method for analysing printing ink due to its rapid testing and low associated costs [7]. In terms of precision, both techniques provided comparable precision figures for inkjet ink (10% - 15%) but toner ink (3% - 27%) gave poorer results due to its larger variations.

Despite low repeatability between measurements, good discrimination for these inks can be accomplished with both techniques. Haase *et al.,* [68] applied ATR-FTIR spectroscopy and LIBS to analyse pharmaceutical packages. They discovered that the information from ATR-FTIR spectroscopy was complementary to LIBS. ATR-FTIR provided information from organic constituents, while LIBS revealed the presence of inorganic elements in the samples. However, several peaks from the inorganic composition can appear in ATR-FTIR spectra in the regions from 1000 cm^{-1} to 400 cm^{-1}. Król *et al.,* [62] compared the performance of LIBS against µXRF in the ink analysis of banknote papers. They determined that the same measuring area of banknote papers displayed strongly varied elemental compositions from each instrument. The distinction between these two techniques was likely caused by the differences in penetration depth and sensitivity. As shown in Table 3, the iron content in toner ink samples aids in the subclassification of these samples into mono-component and two-component toners using SEM-EDS. Mono-component toners comprise around 30% to 70% magnetite, which are higher compared to two-component toners.

Table 3
Comparison of LIBS with other spectroscopic techniques in analysing printing ink

Other spectroscopic technique	Sample	Findings	Ref.
LA-ICP-MS	Toner, inkjet, offset, and intaglio ink on paper	LIBS could not detect all elements found by LA-ICP-MS. However, LIBS detected problematic elements (i.e., Si, Ca, K) and additional elements that can discriminate indistinguishable samples in LA-ICP-MS. Lesser interferences and improved signal-to-noise ratio for Fe, Ca, K, and Si in LIBS. Both techniques showed comparable precision figures for inkjet ink (10-15%) but poorer results for toner ink (3-27%). Tandem LIBS-LA-ICP-MS system reduced interferences and improved discrimination ability.	[7,73]
µXRF analysis	Ink on banknote papers	The same measuring area showed strongly varied elemental compositions from µXRF analysis and LIBS.	[62]
ATR-FTIR spectroscopy	Ink on pharmaceutical packages	Information from LIBS and ATR-FTIR were complementary. LIBS provided inorganic elemental information. ATR-FTIR revealed the presence of organic compounds.	[68]
SEM-EDS	Toner and inkjet inks on paper	Low discrimination was observed for inkjet (47.4%) and toner (70.7%) ink samples, indicating that SEM-EDS has lower sensitivity as compared to LIBS and LA-ICP-MS. SEM-EDS subclassified toner ink according to their iron composition, which categorised the samples into mono-component and two-component toners.	[7]

6. Merging LIBS with Multivariate Data Analysis

Multivariate data analysis is the application of statistical tools combined with scientific studies to improve sample discrimination and produce extensive data. Manual processing of datasets from LIBS can be impractical due to the combined complexities and sheer volume of chemical information in the spectra (sometimes more than 500 spectra lines), especially with many samples [61,64,68,75,78]. However, systematic classification of samples can be accomplished by introducing chemometric analysis to the data [68,75]. The chemometric analysis can extract valuable information based on the differences among the acquired spectra. This analysis is advantageous for printing ink analysis since it reveals minimal differences between ink samples with the return of higher accuracy for ink discrimination. A summary of applied statistical analyses in previous studies is shown in Table 4.

Table 4
List of statistical analyses applied with LIBS for printing ink analysis

Statistical analysis	Findings	Ref.
Principal Component Analysis (PCA)	Good separation and variation (beyond 95%) were observed for toner and inkjet ink. Significant information from ink manufacturers and a large sampling collection were necessary for sample classification. PCA reduced variables before classifications with supervised machine learning models.	[1,2,7,68]
3-sigma criterion	Excellent discrimination was achieved for toner ink samples (97%) and inkjet ink samples (93%).	[1]
Pairwise comparison analysis	Excellent discrimination for toner (98%) and inkjet (100%) samples was achieved using Analysis of Variance (ANOVA) with Tukey's post hoc test.	[1]
t-test	Three indistinguishable pairs of toner samples were discriminated with a 95% confidence limit.	[1]
Classification models	Robust classification models of Linear Discriminant Analysis (LDA) and *k*-Nearest Neighbor (KNN) were obtained using data fusion of ATR-FTIR and LIBS with low confusion rates and error. The models showed high accuracy with correct classification rates for LDA (85-99%) and KNN (90-100%).	[68]
Discriminant analysis	Advanced multivariate discriminant analysis of multivariate curve resolution – alternating least square/discriminant analysis (MCR-ALS/DA) resulted in accurate and reliable results. Better results for print identifications were presented in the UV range (83%) compared to ranges of Vis (60%) and UV-Vis (71%).	[72]

Lower standard deviation values were obtained using datasets from µXRF analysis (approximately 20%) in comparison to LIBS (approximately 28%) when taking into consideration the quantitative repeatability of these methods [62]. Therefore, the repeatability of LIBS is slightly lower than µXRF. Principal Component Analysis (PCA) was applied for toner and inkjet ink samples. It was found that PCA offered good separation and variation (beyond 95%) between brands and models of these samples [1,2]. PCA required an extensive sampling collection, as highlighted by Trejos *et al.,* [7]. On top of the sampling requirement, a systematic grouping of printing ink based on their source and brand requires the necessary information from the manufacturers of the ink.

Haase *et al.,* [68] implemented PCA before classifications using LDA and KNN. PCA reduced the variables to be used as data input for these supervised machine-learning models. The classifications with KNN and LDA were realised by combining the data from ATR-FTIR and LIBS. The hybrid information produced robust classification models with low error and confusion rates. These models had high accuracy, as observed in the classification rate for both LDA (85% - 99%) and KNN (90% - 100%). In contrast to models from separate datasets, lower percentages were observed in LIBS datasets, with 69% to 94% for LDA and 74% to 97% for KNN. ATR-FTIR datasets gave outputs of 81% to 95% and 88% to 99% for KNN and LDA, respectively. Excellent discrimination was achieved for toner (97% with five indistinguishable pairs) and inkjet (93% with one indistinguishable pair) samples on paper when the 3-sigma criterion was employed [1].

Applying a pairwise comparison analysis namely ANOVA with Tukey's post hoc test efficiently discriminated toner and inkjet ink samples with 98% and 100% discrimination, respectively. The three indistinguishable pairs of toner ink samples were discriminated using a student t-test at a 95% confidence limit. The technique of MCR-ALS/DA acquired reliable and accurate results, as conducted by Metzinger *et al.,* [72]. Better results were observed in the UV range for print identifications compared to ranges of Vis and UV-Vis. This is proved by a higher percentage of accuracy in the UV range at 83% with 40 out of 48 correct identifications. As for the rest of the spectral ranges, the Vis range had an accuracy of 60%, while the UV-Vis range was accurate by 71% for print identifications. UV range showed low spectral background and number of peaks resulting in highly distinctive spectral features. Therefore, better results were observed in MCR-ALS/DA approach by using the UV range.

7. Conclusions

Analysing printing ink may be more complex than pen ink because of the broader variability of compounds that are present in the printing ink. The implementation of spectroscopy analysis, including LIBS, has garnered attention among forensic scientists. This review article discusses the strengths and limitations of this technique in the analysis of printing ink. Although LIBS' applications are still in their infancy, the reliability of LIBS to distinguish printing ink samples qualitatively and quantitatively has been peer reviewed in a few studies. LIBS provides essential information on printing ink to support the results of organic constituents from ATR-FTIR spectroscopy while overcoming the analytical limitations of other techniques (LA-ICP-MS). Furthermore, LIBS showed promising results when coupled with statistical analysis that yields higher accuracy for ink discrimination. Future research can be narrowed to the application of LIBS in conjunction with spectroscopic and statistical techniques that have not been previously explored. The application of LIBS to analyse other questionable printed documents, such as travel and identity documents, can be explored for good measure.

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