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Forensic analysis of printing inks using tandem Laser Induced Breakdown Spectroscopy and Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT

Elemental analysis, using either LA-ICP-MS or LIBS, can be used for the chemical characterization of materials of forensic interest to discriminate between source materials originating from different sources and also for the association of materials known to originate from the same source. In this study, a tandem LIBS/LA-ICP-MS system that combines the benefits of both LIBS and LA-ICP-MS was evaluated for the characterization of samples of printing inks (toners, inkjets, intaglio and offset.). The performance of both laser sampling methods is presented. A subset of 9 black laser toners, 10 colored (CMYK) inkjet samples, 12 colored (CMYK) offset samples and 12 intaglio inks originating from different manufacturing sources were analyzed to evaluate the discrimination capability of the tandem method. These samples were selected because they presented a very similar elemental profile by LA-ICP-MS. Although typical discrimination between different ink sources is found to be >99% for a variety of inks when only LA-ICP-MS was used for the analysis, additional discrimination was achieved by combining the elemental results from the LIBS analysis to the LA-ICP-MS analysis in the tandem technique, enhancing the overall discrimination capability of the individual laser ablation methods. The LIBS measurements of the Ca, Fe, K and Si signals, in particular, improved the discrimination for this specific set of different ink samples previously shown to exhibit very similar LA-ICP-MS elemental profiles. The combination of these two techniques in a single setup resulted in better discrimination of the printing inks with two distinct fingerprint spectra, providing information from atomic/ionic emissions and isotopic composition (m/z) for each ink sample.

1. Introduction

The improvements in computer hardware, software and high-quality commercial printers have facilitated the fraudulent use of authentic documents and the counterfeiting of documents [1,2]. The chemical characterization of printing inks can aid forensic document examiners to both discriminate between different sources of printers and, equally important to associate documents that have originated from the same printing source.

Conventional methods used for the examination of printing inks include macroscopic/microscopic examinations, visible, IR and UV imaging techniques (i.e. Visual Spectral Comparator), Thin Layer Chromatography (TLC) [3], XRF (X-ray fluorescence) [4], Scanning Electron Microcopy (imaging and EDS analysis) [5], Pyrolysis Gas Chromatography (Pyr-GC) [6] and Raman spectroscopy [7–9]. The majority of these methods are good for screening proposes and can provide qualitative information regarding the chemical composition of printing inks. These methods can also assist with the identification of counterfeit documents and to discriminate between documents originating from different printing sources. The availability of advanced software and high quality printers has necessitated the development of more sensitive and robust techniques for the detection of fraudulent activities related to printing inks and to improve the tools needed to associate documents originating from the same source [2].

The chemical composition of inks can be categorized into two major parts: the organic components and the inorganic components. Novel methods for the analysis of organic constituents involve chromatographic methods, FTIR, Raman spectroscopy, DART-MS (Direct Analysis in Real Time Mass Spectrometry) and desorption/ionization mass spectrometry [7,10–16].

The inorganic portion of the ink can be a valuable tool for the characterization and discrimination of printing inks however there are very few publications describing its utility and it is often underutilized in document examinations [17–22]. It has been reported that a variety of elements are used in driers, charge control agents, additives, pigments, and dyes, during the manufacturing process to provide specific

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properties to the ink pertaining to dryness, flexibility, gloss, and color [23]. Ink manufacturers use a distinctive combination of the inorganic components, which can make it possible to distinguish formulations among manufacturing sources and even between batches of the same manufacturer over different manufacturing dates. The main purpose of this study is to use tandem LIBS-LA-ICP-MS to characterize printing inks based on their elemental profiles as a means to improve the characterization, confirmation and discrimination potential of conventional methods, such as SEM-EDS and μ-XRF.

Recent advances in rapid solid sampling of materials using laser ablation (LA) coupled to inductively coupled plasma mass spectroscopy (ICP-MS) have led to this analytical method to be regarded as the "gold standard" in the field of elemental analysis for trace level components in solids. Another emerging analytical technique that uses laser ablation is Laser Induced Breakdown Spectroscopy (LIBS). Both of these techniques have been incorporated into a single commercial instrument so that LA-ICP-MS and LIBS are now possible for ink analysis, simultaneously, for the first time.

A tandem LIBS/LA-ICP-MS setup combines the benefits of the two individual techniques. LIBS utilizes the characteristic photons generated during the relaxation of the excited neutral and ionic species to create a spectral signature of the elements. A mass spectrometer coupled to an ICP results in mass to charge ratios characteristic of the elemental composition of the ejected particles resulting from the laser–material interaction. The advantages of this combination include rapid screening (LIBS) and confirmation (ICP-MS) of the elements, simultaneously. LIBS can be used to quickly create an elemental menu for ICP-MS analysis and the ICP-MS data can be used to select a suitable internal standard to normalize the LIBS data [24].

The total amount of sample consumed is less when compared to the sample introduced to LIBS and LA-ICPMS in two separate experiments and the total analysis time is shorter as both phenomena are monitored simultaneously in tandem LIBS/LA-ICPMS. In real world scenarios for forensic cases where the sample for analysis may be insufficient for two separate techniques, a tandem mode is favorable.

These two methods also complement each other in several ways. Elements like Sulfur, Calcium, Iron, Potassium and the halogens are very difficult to detect and confirm using standalone ICP-MS because of the spectral interferences (isobaric and polyatomic) involved but the emission lines resulting from these elements are distinct in LIBS. Elements present at trace levels (<10 ppm) are difficult to detect using standalone LIBS while LA-ICP-MS has detection limits in sub-ppm levels. This makes LIBS inadequate when trace elements have to be detected, and high degree of certainty is sought. Alternatively, major elements present at higher concentrations (%wt) can be monitored by LIBS instead of LA-ICP-MS to protect the ICP-MS detector. Under standard acquisition conditions, it is difficult to detect the isotopes of elements using LIBS alone while ICP-MS can provide clear information about the different isotopic signatures of an element, providing unambiguous identification. Thus, the combination of these two techniques makes it possible to detect most of the elements in the periodic table and increases the detection reliability as well.

LIBS has been used for the forensic analysis of gel inks, printing inks and paper [21,22,25]. The notable advantages of LIBS over ICP-MS are of its relatively cheaper cost, potential for miniaturization, possibility for remote and in-situ analysis [26]. Laser ablation ICP-MS and LIBS have been found to be effective for several applications in the areas of trace evidence and environmental forensics [27–31]. These two techniques have been used together for simultaneous elemental imaging in plants [32], alloys [24], and rocks [33,34], recently, for the examination of documents using paper substrates, writing inks and printing inks as the sample matrix [21,22]. The present study is focused on the development and design of a comprehensive tandem LIBS/LA-ICP-MS method that is well suited for the chemical analysis of printing inks and can be possibly incorporated into use by forensic laboratories as an additional tool for the chemical characterization of these samples.

2. Experimental section

2.1. Instrumentation and measurement parameters

2.1.1. Experimental setup for LIBS

The LIBS used in this study (J-200) consisted of a 266 nm ns-Nd:YAG laser with a 6-channel broadband spectrometer (190 nm to 1040 nm) with a resolution of <0.1 nm or less in the UV to mid VIS range and 0.12 nm or less in the mid VIS to NIR range. The photon detector has a CCD linear array (Avantes, Broomfield, CO) with a variable stage velocity and gate delay adjustment from 50 ns to 1 ms with 25 ns step resolution and a fixed integration time of 1.05 ms. The software includes the Axiom LA, TruLIBS™ emission database and Aurora data analysis (Applied Spectra, CA). Table 1 shows the optimized LIBS parameters for the tandem setup.

2.1.2. LA-ICP-MS setup

The LA-ICP-MS analyses were conducted using a quadrupole ELAN DRC II (Perkin Elmer LAS, Shelton CT USA) coupled to the same laser ablation system described above. The elemental list consisted of ^{7}Li, ^{23}Na, ^{24,25}Mg, ^{27}Al, ^{29}Si, ^{34}S, ^{39}K, ^{42}Ca, ^{45}Sc, ^{47,49}Ti, ^{52,53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60,62}Ni, ^{63,65}Cu, ^{64,66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{103}Rh, ^{137}Ba, ^{139}La, ^{140}Ce, ^{142,143}Nd, ^{180}Hf, $^{182–184,186}$W, and ^{206,207,208}Pb. The elements listed in this menu have intensities that are significantly higher than the paper background substrate and are also above the limits of detection. Hence, these elements were chosen for discrimination purposes. The use of elements such as Zr, Rh, Hf, and W in ink formulations has been described in the literature [35–37]. The listed elements were found to have good reproducibility (<10% RSD), and were found to be present above their LODs. Also these elements provided minimum variation within the same source and maximum variation between sources. All the measurements were taken using data acquisition in scan mode from m/z 6 to m/z 238. Scanned regions that were expected to have large isobaric contributions from Argon isotopes and other polyatomic interferences were excluded in the scan method. The isotope ratio for each element based on their natural abundance was used to confirm the presence of that element.

2.1.3. Tandem LIBS-LA-ICP-MS setup

Standalone LIBS and LA-ICP-MS described above were combined together in a single setup as shown in the Fig. 1.

A 266 nm (ns) laser was focused onto an ink sample placed in a sample cell and the light emitted by the excited species in the LIBS plasma was collected by a fiber optic connected to a CCD spectrometer. Simultaneously, the ablated particles were carried to the ICP using Ar carrier gas. Fig. 1 depicts the simultaneously collected and actual mass spectrum (left) and the respective LIBS spectrum (right) for an ink sample containing 10,000 ppm of 10 different elements including Fe, Ca, Sr, Mn, Na, Li, K, Cu and Zn using a tandem LIBS-LA-ICP-MS setup. The signal/noise for the elements K, Ca and Na is greater in the LIBS spectrum than in the LA-ICP-MS spectrum. Multiple emission lines as points of comparison can be appreciated in the LIBS spectrum for problematic elements such as Si, Fe, and Ca, which suffer from isobaric and polyatomic interferences in ICP-MS.

Table 1
Optimized instrumental parameters for the analysis of printing inks.

Parameters	Inkjets	Toners	Offset	Intaglio
Ablation mode	Single line	Single line	Single line	Single line
Laser spot size	200 μm	200 μm	200 μm	200 μm
Frequency	0.8 Hz	1.8 Hz	4 Hz	4 Hz
Laser energy	40% (7.8 mJ)	70% (13 mJ)	20% (4.1 mJ)	20% (4.1 mJ)
Ablation rate	50 μm/s	40 μm/s	30 μm/s	30 μm/s
Gate delay	0.1 μs	0.8 μs	0.1 μs	0.1 μs
Argon flow in the cell	0.9 L/min	0.6 L/min	0.7 L/min	0.75 L/min

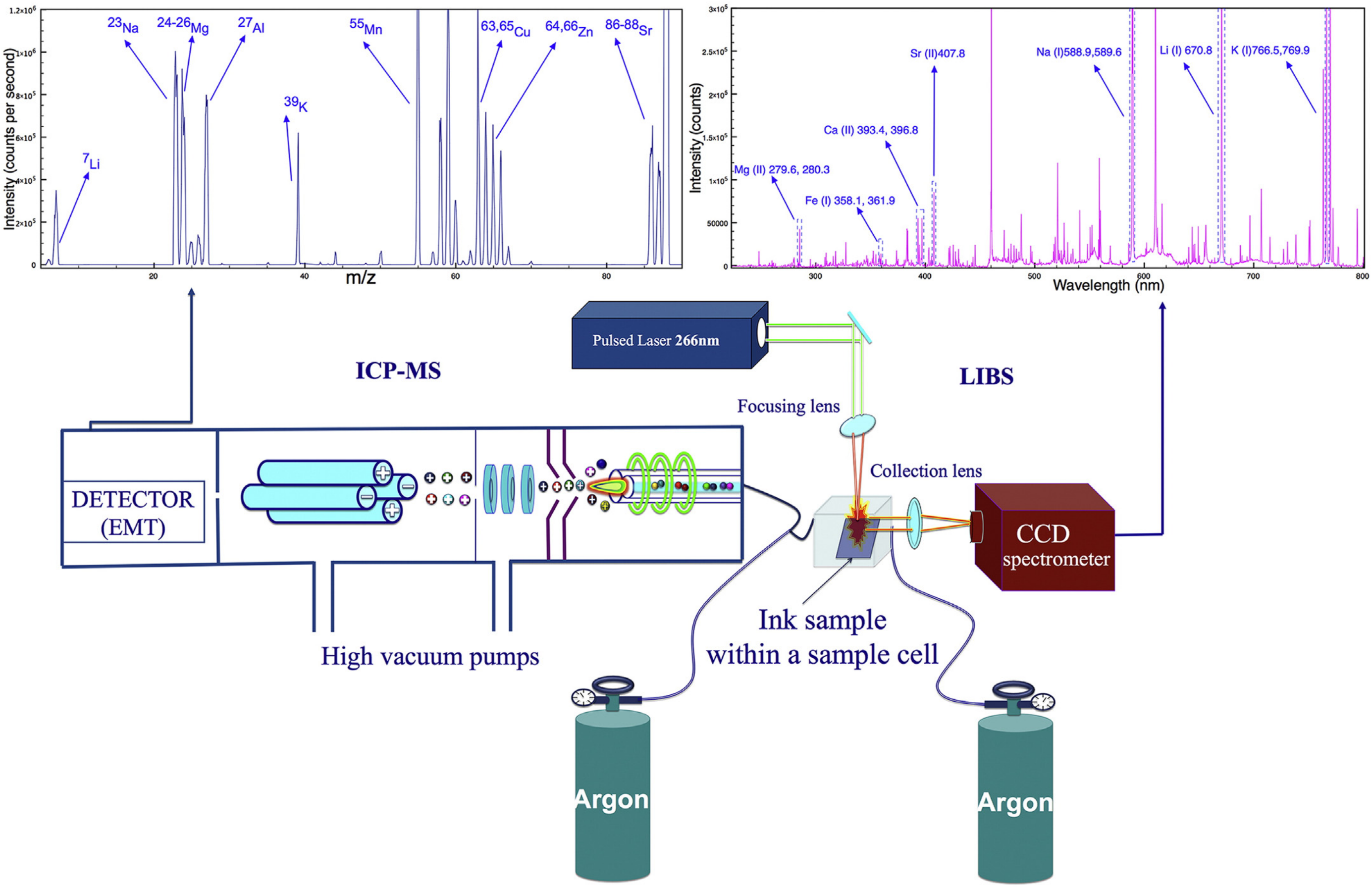

Fig. 1. Schematic diagram of a tandem LIBS-LA-ICP-MS showing the actual spectra (ICP-MS on the left and LIBS on the right) for an ink sample containing 10,000 ppm of a selected element list (Fe, Ca, Sr, Mn, Na, Li, K, Cu and Zn).

2.2. Reagents and standards

A 10,000 ppm (CPI, International USA) of a standard solution containing Al, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Na, Sr and Zn was diluted to different concentrations ranging from 100 to 10,000 ppm. One microliter of each solution was spiked onto a Whatman paper (grade 42) and allowed to dry at room temperature. Whatman paper was selected as a substrate to reproduce substrate conditions used for the printouts. The spiked sample was then used to check the performance, for optimization, and to construct calibration curves and for the calculations of limit of detections.

2.3. Sample preparation and sample collection

Printing ink samples were printed directly on Whatman paper (grade 42 (Whatman Ltd)) as previously reported [22]. The printout consisted of one of the two formats, either a word document template with numbers and letters in Times New Roman size 12 or a test page format assigned by default of each printer. To ensure that all the printouts were collected from pure color cartridges (Cyan, Magenta, Yellow and Black) they were inspected using an optical microscope. No contamination from other (color) ink cartridges was found. For those inks lacking a printer model, a manual deposition method was employed. For inkjets, about 5 μL of the ink was removed from the cartridge and deposited onto the Whatman 42 paper and left to dry at room temperature. For toners, the manual deposition method consisted of depositing a small amount of toner powder and rolling it onto a paper substrate while melting at about 140–180 °C to create a smooth and uniform toner layer. Intaglio inks were collected from bank notes. The Keesing Documentchecker (Keesing reference systems Inc) was used to identify the intaglio printed ink areas, and further verification of the intaglio ink was done by the use of a Keyence 3-D microscope. The intaglio printed region was then carefully cut and analyzed without any sample preparation.

Offset samples were collected in printed form (3 samples), obtained from Lincoln visa (2 samples) and as a paste (7 samples). For raw paste samples, they were first homogenized with a vortex mixer, followed by deposition onto Whatman paper forming a thin layer on the paper. These samples were then dried at room temperature and analyzed.

A set of more than 50 toners and inkjet printing inks was previously characterized in our group by LA-ICP-MS and LIBS separately while 86 intaglio and 79 offsets were analyzed by standalone LA-ICP-MS only. From this collection, a subset of inks that showed similar LA-ICP-MS signatures was selected. The sample set consisted of 9 black toners from 4 different brands, 10 inkjets of four different colors (CMYK) from 6 different brands, 12 offsets and 12 intaglio from different sources.

3. Results and discussion

3.1. Development and optimization of the Tandem LIBS-LA-ICP-MS method for the analysis of printing inks

LIBS and LA-ICP-MS both operate under different principles and therefore they are optimized differently when operated in standalone mode in comparison to tandem mode. For LIBS the most important factor is the efficient excitation of the atomic and ionic species and their subsequent correct timing for collection of the emission lines; while for the mass spectrometry the production of sub-micron sized particles with efficient particle transport to the ICP plays the most critical role.

Some factors such as the gas environment affect the shape, size and duration of the microplasma as well as the LIBS spectral background. The gas environment has also shown to have a direct effect on the particle size and distribution of the particles generated during the ablation process [38,39]. In LIBS, ideal conditions should provide a long and stable microplasma while in LA-ICP-MS the instrumental parameters should provide a fine and uniform aerosol traveling with uniform velocity to the ICP plasma [40,41].

Unfortunately, some gases and their flow may enhance the LIBS and LA-ICP-MS signals in opposite directions. For example, in LIBS the gas conditions are selected to increase the plasma duration while in LA-ICP-MS the gas conditions are aimed to reduce plasma duration to improve particle formation.

As a consequence, when LIBS and LA-ICP-MS are operated in tandem mode, some instrumental conditions must be compromised to offer an acceptable analytical signal for simultaneous acquisition using both methods.

Since LA-ICP-MS is at least one order of magnitude more sensitive than LIBS, the approach that was followed was to optimize first the acquisition parameters for LIBS and then adjust them to LA-ICP-MS, therefore at the end we gave up some ICP-MS sensitivity to gain dual simultaneous information with good precision for both methods.

The deposition of ink during the printing process is different for all the four different types of printing inks. Toner, intaglio and offset inks are slightly raised above the paper substrate while inkjet ink is mostly embedded in the paper fibers. Moreover, their chemical composition is also different, with major differences in their organic and inorganic constituents affecting the laser to sample interaction. As a result, all the four printing ink types were separately optimized for the laser parameters such as frequency, ablation rate and energy. It is desirable to use enough energy to ablate the ink off the paper with minimal destruction to the paper substrate; hence the laser energy used was adjusted such that no significant paper mass was removed during the ablation process. The signal intensity, signal to noise ratio (S/N) precision (%RSD) and the extent of paper contribution were the main parameters used for the method optimization. Intensity of signals increased with the increase in the laser energy, but this also increased the paper contribution. The laser energy was varied from 10% to 80%. For lower laser energy, high background noise was detected. Also, peaks at lower wavelength were suppressed at energies below 25%. The laser energy that yielded peaks significantly higher than the background with minimal damage to the paper for both at lower and higher wavelengths were found to be 40% for inkjets (22.4 J/cm^2), 70% (37.6 J/cm^2) for toners, and 20% (12.2 J/cm^2) for both intaglio and offset inks. Using these energies, the spot sizes were varied from 100 μm to 200 μm. The penetration was found to be deeper for 100 μm spot size and also more damage to the paper substrate was detected while 200 μm spot size caused less damage to the paper. Also to account for the sample heterogeneity, a large laser spot size (200 μm) was used for all experiments. The line ablation mode was found to provide adequate precision. Helium and Argon were both tested as an ambient gas for LIBS and also as a carrier gas for LA-ICP-MS. The gate delay for the CCD was varied from 0.05 to 3 μs using both Argon and Helium. The signals at lower emission wavelength like Fe 358.1 and 361.9 nm were found to be suppressed when a longer gate delay (>1 us) was used while peaks at longer wavelengths like K 766.5 nm and 769.9 nm were found to be suppressed at shorter gate delays (<1 us). At all gate delays Argon proved superior to Helium in terms of signal intensity and signal to noise ratio for LIBS. Higher emission peaks were observed in Argon atmosphere in LIBS at the cost of a lower signal in the mass spectrum. Argon was selected as an ambient gas for LIBS and as carrier gas for the LA-ICP-MS experiment. The flow of ambient gas also affected both the emission and the m/z spectra. Higher flow rates were not suitable for mass spectrum, while lower Ar flow rates would suppress the emission spectrum. The gate delay and flow rate were optimized to 0.8 μs, 0.6 L/min and 0.1 μs, 0.9 L/min for toners and inkjets respectively. For offset and intaglio 0.1 μs gate delay was found to be optimum with 0.7 and 0.75 L/min of Ar gas flow rate respectively. Higher laser frequency (1.8 Hz) was found to be favorable for toners while a relatively lower laser frequency (0.8 Hz) provided better results for inkjets while a higher frequency (4 Hz) could be applied to the offsets and intaglio which can be attributed to the fact that inkjets are embedded in paper, so a higher frequency would cause more damage to the inkjets while for toners, offsets and intaglio which are slightly raised above paper, a higher frequency would not cause any significant damage to the paper inks. The stage linear velocity was also adjusted for toners (50 μm/s) and inkjets (40 μm/s). Similarly the rate of Argon flow also influenced the signals of the inks. The flow rate of 0.6 L/min was found to produce better results for toners while for inkjets, the flow was increased to 0.9 L/min for optimum results.

3.1.1. Comparison of printing inks using LA-ICP-MS and LIBS

Full mass spectra were collected from m/z 6 to m/z 238 except certain isotopes such as (^{12}C), nitrogen isotopes (^{14}N, ^{15}N, ^{14}N^{14}N), oxygen species (^{16}O, ^{17}O, ^{18}O, ^{16}O^{16}O), argon isotopes (^{36}Ar, ^{38}Ar, ^{40}Ar) and major polyatomic interferences (^{40}Ar^{16}O, ^{40}Ar^{40}Ar and all the ^{n}Ar^{n}Ar isotopic combinations from m/z^{n+n} 72 to 80) were not selected for detection during the scanning method to prevent detector saturation. It was hypothesized that potassium could be an important discriminator for printing inks so the resolution of the ^{39}K peak was customized to 0.4 amu to minimize interferences from Ca and Ar isotopes. For the rest of the elements and their isotopes the default quadrupole resolution of 0.7 amu was used. Fig. 1 shows an example of a tandem LIBS-LA-ICP-MS experiment, with two fingerprint spectra, mass spectrum (left) and LIBS emission spectrum (right).

The normalization procedure has been described in a previous publication [22], which consists in dividing the intensity at each data point by the sum of the total intensities from the spectra. This improved the precision between the replicates and also minimized the laser shot to shot fluctuations and differences in the total mass ablated. The minimum threshold for each signal was set as 3 times the signal to noise ratio (SNR); where the signal is defined as the peak of the element in the ink spectrum while noise is defined as the signal contribution from the paper substrate. All the signals in inks were paper background subtracted thus ensuring no paper contribution for the data analysis.

This study showed that the inkjet set contained relatively fewer elements as compared to toners, offset and intaglio. Lithium was detected in inkjets only, which has been reported to be used for electrical conductivity for inkjet printing methodology [42]. Na was present in all of the inkjets while K was the second most frequently occurring element in this set. For the toners set, some other elements besides Na, K and Ca were also detected. Elements like Mn, Fe, Ti, Zr, Nb, Sn, Hf, and Sr were also detected in this toner set as a result of the different

Table 2
Limit of detection (LOD) values in parts per million (ppm) for different elements when operated in tandem mode.

Element	LA-ICP-MS	LIBS
Li	0.7	3.4
Na	79.2	36.4
Mg	17.0	32.0
Al	29.3	102.8
K	33.8	7.7
Ca	393.9	58.3
Mn	0.6	133.5
Fe	30.3	190.9
Ni	1.2	150.4
Co	0.2	38.0
Cu	9.9	61.3
Zn	5.5	94.3
Sr	4.0	7.2

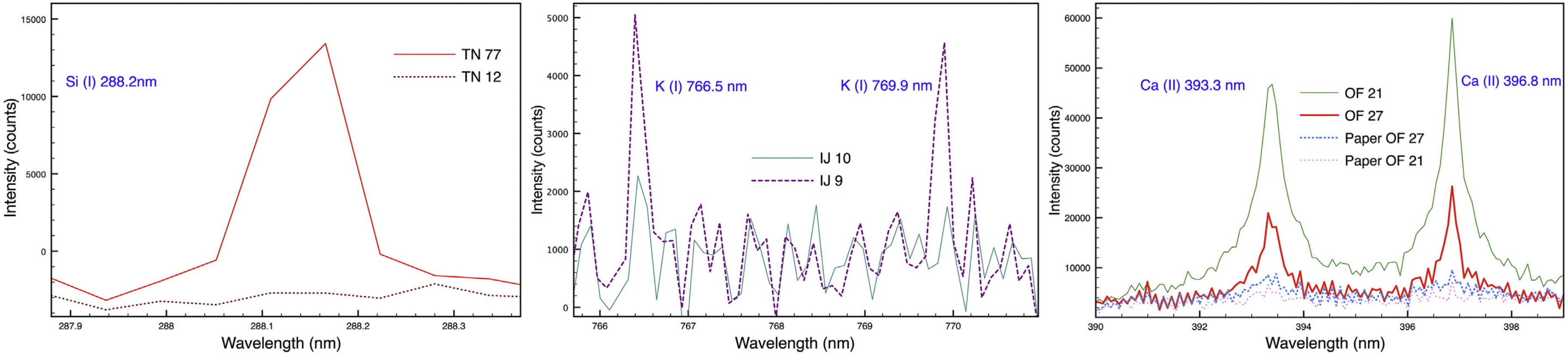

Fig. 2. Emission line peaks for Si (left) in toners (TN 77 vs TN 12), K (center) in inkjets (IN 9 vs IN 10) and Ca (right) in offsets (OF 27 vs OF 21).

formulations in the different printing inks. The use of elements like Zr, Nb, and Hf has been described in various patents and books [35,43].

Pairwise comparisons were used to compare all the toner samples to each other and all the inkjet samples to each other in the same manner as previously reported [22]. For this analysis, all the replicates of the spectra for each sample were overlaid on top of a comparison pair and a decision as to match/no match was made depending on the extent of overlap between the replicates and within the replicates. When the extent of overlap between samples was greater than the overlap within the replicates, the two samples were determined to be "discriminated". Samples with low overlap (same overlap between samples as between replicates) were determined to be "associated". The presence or absence of a certain elements was also used to discriminate between samples.

There are some drawbacks to using a quadrupole mass analyzer as it can only separate ions that are one mass unit apart and argon based inductively coupled plasma contains isobaric and polyatomic interferences. Because of the isobaric interference of Argon at mass 40 (^{40}Ar) and the presence of polyatomic interferences such as ^{39}Ar^{1}H, formed in the ICP, the isotope ^{40}Ca is not detected using a standard quadrupole mass spectrometer. Similarly, the most abundant isotope of iron (^{56}Fe) suffers a polyatomic interference from Argon oxide (^{40}Ar^{16}O), while ^{28}Si has a major interference from ^{14}N^{14}N. So these mass regions were avoided and less abundant isotopes such as ^{44}Ca (2.1% abundance), ^{29}Si (4.7% abundance) and ^{57}Fe (2.2% abundance) were monitored during the analysis in the mass spectrum. Potassium, which has previously been reported to be a useful discriminator for printing inks [22] represents another challenge for ICP-MS measurements due to the isobaric interferences of its major isotope (^{39}K) with Argon (^{39}Ar), and polyatomic interference from ^{38}Ar^{1}H. Moreover, other low abundant potassium isotopes ^{40}K and ^{41}K also suffer from interferences. Fortunately, multiple emission lines for these elements (Ca, Fe, and K) can be easily detected by LIBS with few interferences in the emission spectrum.

3.1.2. Calibration curves and limits of detection

Due to the lack of standard reference materials for inks, quantitative analysis by LIBS and LA-ICP-MS is still a challenging task. Standard solutions of different concentrations ranging from 100 ppm to 10,000 ppm were prepared to evaluate the analytical performance of the methods developed. One microliter of the standard was spiked onto a Whatman paper substrate and allowed to dry overnight. The dried samples were then subjected to tandem LIBS-LA-ICP-MS using the optimized parameters. Calibration curves were built using the peak areas (integrated peak areas minus the background). The calibration curves of different elements obtained through the mass spectra and the emission spectra were linear and reproducible with R^2 values better than 0.99 and RSD's less than 10% for most of the elements.

Four replicates were measured at each concentration in the calibration curve. The m/z ratio and the emission lines were chosen to minimize spectral interferences. The LODs were calculated as previously reported [22] and shown in Table 2. The limit of detection ranges from subparts per million to hundreds of parts per million for both LIBS and LA-ICP-MS. The LODs for LA-ICP-MS in tandem mode are at least one order of magnitude higher as compared to the previous studies conducted using the standalone LA-ICP-MS [22] while the precision was below 10% for most of the elements for both LIBS and LA-ICP-MS. This is a consequence of the compromised parameters selected in tandem mode that sacrificed some sensitivity for LA-ICP-MS measurements. For elements like Ca and K, the limits of detection were found to improve when LIBS was used because the most abundant isotopes for these elements suffer from isobaric interferences from Argon isotopes in mass spectrometer, while these elements are relatively good emitters in LIBS.

3.2. Complementary information from tandem LIBS and LA-ICP-MS

Significant differences were detected between toners and inkjets of the same color by both LA-ICP-MS and LIBS. Nonetheless, LIBS provided additional discrimination to LA-ICP-MS only for some specimens. Fig. 2 provides two examples of gained discrimination using LIBS for the detection of elements such as Si in toners, K in inkjets and Ca in offsets. Significant and reproducible differences in the content of these elements were detected in the emission spectra of LIBS, while they would remain indistinguishable by LA-ICP-MS alone.

For the pairs that were indistinguishable by LA-ICP-MS, LIBS was able to detect some additional elements, which were found to be useful for discrimination. Table 3 shows the different elements that could be detected using LIBS and LA-ICP-MS and some additional elements that were detected by LIBS. As previously reported, fewer elements are detected in the inkjet samples compared to the toner samples as a consequence of their chemical formulations. Most of the elements detected by the two methods are similar but some elements such as Fe, Ca, K, and Si presented less interferences by LIBS, providing better signal to noise and measurement reproducibility hence improving the discrimination capabilities.

Previous studies have shown that overall; LA-ICP-MS results in better discrimination between different inks (>99% of comparison pairs are discriminated) in comparison to LIBS (~89–94% discriminated, depending on the ink type) [21,22]. However, when a set specifically selected based on the lack of discrimination by LA-ICP-MS, LIBS is shown to provide added discrimination. LA-ICP-MS provides superior results in the absence of interferences. When LIBS is hyphenated with ICP-MS, the interferences can be minimized and the discrimination ability is enhanced which was observed through the overall discrimination by spectral overlay. Table 4 summarizes the discrimination of the two methods combined in the tandem system. For inkjets, toners and offsets the discrimination has been increased to a 100%, while one of the intaglio pairs (that were from the same currency of the same country) was not able to be discriminated. The fusion of LIBS with LA-ICP-MS has enhanced the discrimination capability by providing complementary information for elements, which cannot be attained separately by these standalone techniques.

Table 3
List of pairs indistinguishable by standalone LA-ICP-MS and the additional elements detected by LIBS.

Indistinguishable pairs (LA-ICP-MS)	Elements detected by LA-ICP-MS	Additional elements detected by LIBS
IN 4 and IN 9	Na	Ca, K
IN 4 and IN 10	Na	Ca, K
IN 9 and IN 10	Na	Ca, K
IN 56 and IN 57	Na, Al	K
TN 12 and TN 13	Mn, Fe	Na, Ca, K
TN 12 and TN 17	Mn, Fe	Na, Ca, K
TN 12 and TN 18	Mn, Fe	Na, Ca, K
TN 12 and TN 19	Mn, Fe	Na, Ca, K
TN 12 and TN 77	Mn, Fe	Na, Ca, K, Si
TN 13 and TN 17	Mn, Fe	Na, Ca, K
TN 13 and TN 18	Mn, Fe	Na, Ca, K
TN 13 and TN 19	Mn, Fe	Na, Ca
TN 17 and TN 18	Mn, Fe	Na, Ca, Si
TN 17 and TN 19	Mn, Fe	Na, Ca, K
TN 18 and TN 19	Mn, Fe	Na, Ca, K
TN 52 and TN 53	Ti, Zr, Nb, Sn, Hf	Na, Ca, K, Si
OF 21 and OF 27	Mn, Co	Ca
OF 47 and OF 50	ND (not detected)	Na, Ca, K
OF 18 and OF 65	Mn, Co, Cu	Ca, Na
OF 71 and OF 75	Mg, Al	Na, Si
OF 73 and OF 77	Mg, Cu	Na, Ca, Si
OF 74 and OF 78	Mg, Al, Sr, Ba	Si, Ca
IT 10 and IT 11	Mg, Al, Ca, Mn, Co, Sr, Zr, Hf	K
IT 35 and IT 36	Mg, Ca, Ti, Mn, Co, Cu, Zr, Nb, Hf	Na, Ca, K

Table 4
Discrimination of selected printing inks by two methods using spectral overlay.

Ink type	Number of samples	LIBS	LA-ICP-MS	Tandem (fusion of) LIBS/LA-ICP-MS
Toners	9 (36 comparison pairs)	100%	66.60%	100%
Inkjets	10 (45 comparison pairs)	97.80%	91.10%	100%
Offsets	12 (66 comparison pairs)	92.42%	90.90%	100%
Intaglios	12 (66 comparison pairs)	87.88%	96.97%	98.50%

4. Conclusions

A tandem technique (LIBS and ICP-MS) has been successfully used for the analysis of printing inks for the first time. Qualitative and semi-quantitative tandem LIBS-LA-ICP-MS methods have been developed and optimized for the elemental analysis of printing inks. For those samples known to produce indistinguishable LA-ICP-MS spectra (very similar formulations), the ability of LIBS to detect the major and minor elements can provide additional discrimination over a discrimination using only LA-ICP-MS.

Toners, inkjets, intaglio and offsets are found to have different elemental compositions depending upon their source of manufacture. Major, minor and trace elements present in ink samples can serve as good discriminators for all the four different types of printing inks. Lithium, for example, was found only in inkjet samples and the sensitivity performance of LIBS was found to be superior than LA-ICP-MS. Moreover, the application of LIBS was found successful to overcome the spectral interferences of ICP-MS for the elements K, Ca, Si and Fe, which are good discriminators for both types of printing inks. Fusion of LIBS and LA-ICP-MS has proven to provide complementary information, and enhanced discrimination for both types of inks.

The disadvantages of lower sensitivity for LIBS are overcome by LA-ICP-MS while the drawbacks from typical interferences found in ICP-MS are ameliorated by using LIBS. Combining these two techniques has been found to minimize their individual limitations and now provide a more complete and representative chemical characterization of the printing inks.

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