



# 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.

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## 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 Microscopy (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  $\mu$ -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  $^7\text{Li}$ ,  $^{23}\text{Na}$ ,  $^{24,25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{34}\text{S}$ ,  $^{39}\text{K}$ ,  $^{42}\text{Ca}$ ,  $^{45}\text{Sc}$ ,  $^{47,49}\text{Ti}$ ,  $^{52,53}\text{Cr}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{60,62}\text{Ni}$ ,  $^{63,65}\text{Cu}$ ,  $^{64,66}\text{Zn}$ ,  $^{85}\text{Rb}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{90}\text{Zr}$ ,  $^{103}\text{Rh}$ ,  $^{137}\text{Ba}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{142,143}\text{Nd}$ ,  $^{180}\text{Hf}$ ,  $^{182-184,186}\text{W}$ , and  $^{206,207,208}\text{Pb}$ . 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 $\mu\text{m}$	200 $\mu\text{m}$	200 $\mu\text{m}$	200 $\mu\text{m}$
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 $\mu\text{m/s}$	40 $\mu\text{m/s}$	30 $\mu\text{m/s}$	30 $\mu\text{m/s}$
Gate delay	0.1 $\mu\text{s}$	0.8 $\mu\text{s}$	0.1 $\mu\text{s}$	0.1 $\mu\text{s}$
Argon flow in the cell	0.9 L/min	0.6 L/min	0.7 L/min	0.75 L/min

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