

characterization of solids, elimination for the need for chemical procedures for dissolution, minimum consumption of the sample (< microgram), high sensitivity and high selectivity. Although less mature than LA-ICP-MS, LIBS also shares the benefits associated with laser ablation methods with the added advantage of ***improved speed, versatility, ease of operation, affordability and portability.***

Document related crimes are considered the most prevalent form of crime in society and the examination of ink and paper has been the focus of many criminal investigations. In routine document examinations, non-destructive analytical methods such as microscopic and optical techniques are applied first. However, these are often insufficient to identify the inks used to prepare the document or to determine whether questioned pages originate from the same source, or if one or more pages of the document have been fraudulently replaced. Moreover, paper and ink formulations are constantly changing to adjust to market requirements. As a consequence, there is an increased interest in finding alternative and/or complementary methods of analysis for inks and paper to assist document examiners to overcome analytical challenges that otherwise are difficult to address using the conventional methods. For instance, gel pen inks have become a prominent type of ink found in forensic document examinations due to its widespread use and low cost of manufacture. Nevertheless, the analysis of gel pen inks constitute a challenge for the forensic ink examiner since most of the gel inks are difficult to analyze by conventional techniques such as paper chromatography, TLC and capillary electrophoresis. As a result, other non-destructive or less-destructive methods such as Spectral methods (HyperSpectral Imaging), Raman spectroscopy, Infrared Spectroscopy and μ XRF have been recently explored as alternative tools to cope with forensic comparisons of gel inks. The laser-based methods of LIBS and LA-ICP-MS were used in this current study to develop rugged analytical methods for the qualitative and quantitative elemental analysis and comparison of writing and printing inks and document paper. Laser sampling is particularly well-suited for this application since it can provide good spatial resolution (< 40 μ m) for the direct removal and subsequent elemental analysis of very small samples on surfaces such as ink

deposited on a paper substrate while achieving the necessary sensitivity (LOD of most elements ~ 10-50 ppm).

Soil samples can provide important forensic information to associate an individual to a given geographic location or to associate two individuals to an event. LA-ICP-MS elemental characterization of soil has been shown to provide excellent discrimination between soils originating from different geographic locations. The results from the current project suggests that soil samples can be discriminated by geographic location using LIBS even between small distances in a geographic area. This approach to soil analysis and comparison, when combined with existing geochemical data from the U.S. Geological Survey (USGS) provides new tools to the forensic scientist. In addition, a new method using less than 10 mg of soil sample was developed for forensic analysis.

Finally, one key objective of this research was to evaluate the significance of a “match” of elemental composition for these matrices, when samples are determined to be indistinguishable using an optimized methods. Comprehensive sample sets of inks, paper, cotton and soils were collected from a variety of sources and the discrimination capabilities of both laser-based methods were determined and reported in the peer-reviewed literature. Ten (10) publications [1-10] and more than 50 oral and poster presentations by the PI and students describe the results of the research effort, to date. Three of the papers described analysis of inks/paper [1,6,9], four of the papers described soil analysis [2,5,7,10] and 2 of the papers described cotton and other plant analysis [3,4]. One paper was devoted to fundamental studies of laser-based analysis coupled to atomic emission [8] that was then used to better understand LIBS emissions.

Introduction to Elemental Analysis by LA-ICP-MS and LIBS

Laser ablation can be defined as a progressive and superficial destruction of a material by melting, fusion, sublimation, erosion and explosion [11,12]. A typical LA-ICP-MS setup consists of a laser, an ablation cell and the ICP-MS which is used as an ionization source and analyzer. A solid sample is placed inside the ablation cell and a laser beam is focused on the surface of the sample (see figure 1, left side). When the laser is fired, the high-energy interaction between the laser

and the sample surface produces a cloud of very small particles and micro-droplets. These particles are removed from the sampling cell by a carrier gas, usually argon or helium, and are swept into the ICP plasma for atomization, ionization and subsequent analysis. LA-ICP-MS can be considered as a quasi-non destructive method due to the very small quantities (hundreds of nanograms) that are removed from the analytical ablation. Significant advances in the understanding of the processes involved in the laser ablation of solid materials followed by elemental analysis by ICP-MS provide qualitative and quantitative methods that are very mature, accurate, efficient, and sensitive [13-24].

Forensic applications of LA-ICP-MS and LIBS methods in different forensic sub-disciplines such as trace evidence, environmental forensics and toxicology have also been previously reported [25-59]. The right side of the schematic in figure 1 depicts a LIBS system composed of a pulsed laser, focusing optics, ablation cell where the plasma is generated and light collection optics connected to a spectrometer that resolves the light into individual emission peaks representing the elemental composition.

Reference 8 describes a fundamental study of LA coupled to atomic emission spectroscopy that provides insight into the emission phenomena for a more familiar matrix (glass) and was used to later optimize LIBS parameters.

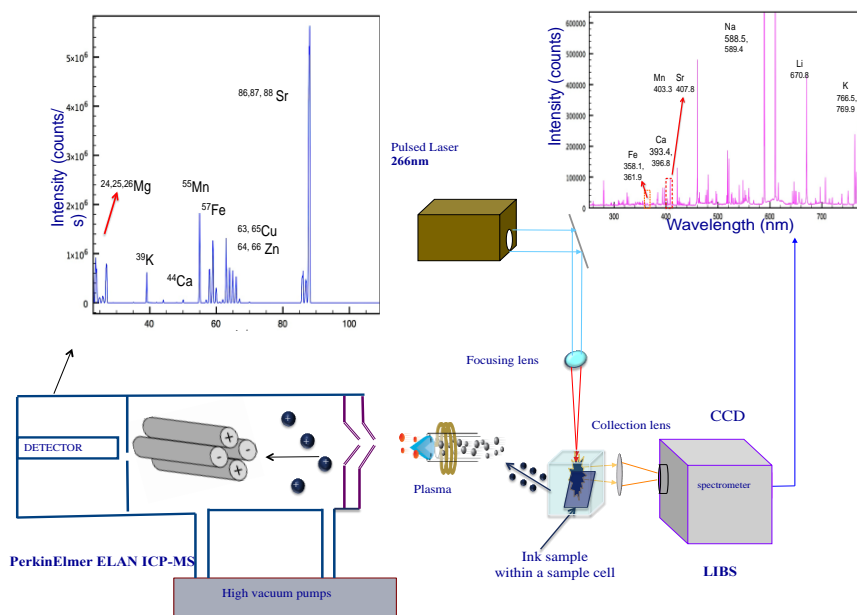


Figure 1. LA-ICP-MS setup (left) and LIBS setup (right). A commercial version of this LA-ICP-MS/LIBS “tandem” system was used to characterize printing inks for this project (from [1]).

Elemental Analysis of Ink and Paper

Inks are usually analyzed in document examinations with the purposes of a) comparing two or more ink entries to determine similarities or differences, b) identifying whether two or more entries were written with the same formula and/or batch of ink and/or c) dating ink entries to determine if documents have been backdated [60]. As ink formulations are continuously changing to adjust to the market requirements there is an increased interest in finding alternative and/or complementary methods of ink analysis to assist document examiners to overcome analytical challenges that are difficult to address using the conventional methods [61-64]. Gel-based and printing inks are examples of inks that benefit from the development of laser-based methods. Calibration curves, using integrated peak areas for each element, have been generated using LA-ICP-MS for the matrix-matched ink standards prepared as discussed in references 6 and 9 printing inks and gel-based writing inks, respectively. Figure 2 is an example of the excellent linearity obtained for LA-ICP-MS for both inkjet and toner standards indicating the feasibility of preparing matrix-matched ink standards without an internal standard.

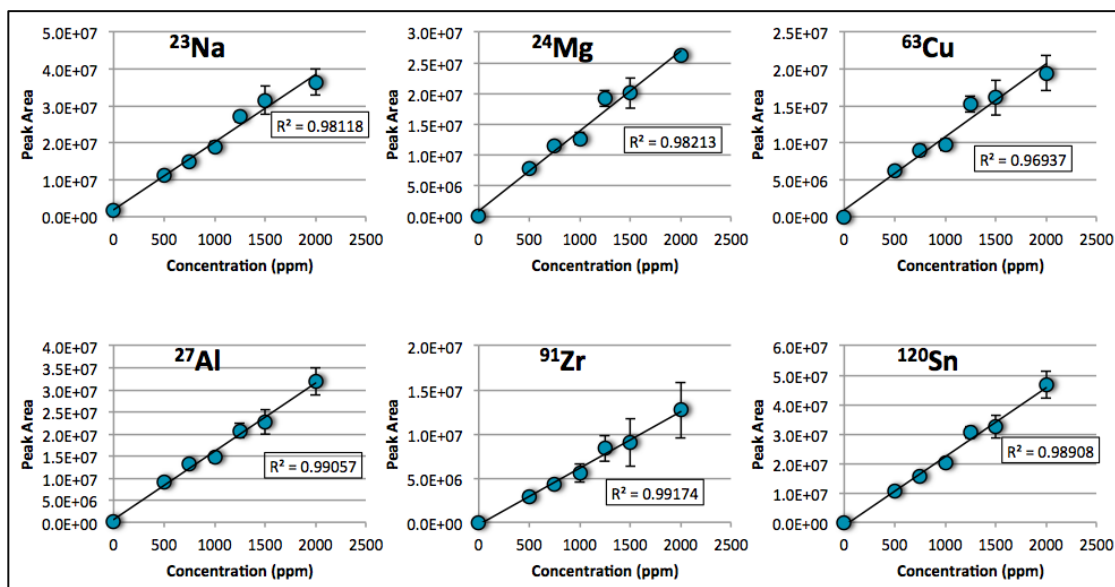


Figure 2. Calibration curves for six isotopes of the matrix-matched inkjet standards; peak areas are not normalized to an internal standard.

All ink samples have been analyzed qualitatively using LA-ICP-MS and SEM-EDS [6]. The discrimination and association potential of the technique was

evaluated using the spectral overlay method described in [6]. LA-ICP-MS provided excellent discrimination for all four ink types while SEM-EDS performed well for toner and intaglio inks, but is limited for the analysis of offset and inkjet inks. Summary results are tabulated below:

Table 1. Discrimination/Association Rates of Printing Inks Using Spectral Overlay of LA-ICP-MS Spectra.

	TONER	INKJET	OFFSET	INTAGLIO
Number of Samples	76	78	79	86
Comparison Pairs	2850	3003	3081	3655
% Discrimination	99.1	99.6	99.8	99.9
Number of Duplicates	24	3	23	6
% Correct Association	92.3	100	99.8	100

A thorough experimental description for the analytical and normalization procedure can be found in reference 9 along with results for gel-based pen inks. A more complete set of experimental/results for the printing inks can be found in reference 6 for LA-ICP-MS and reference 1 for LA-ICP-MS and LIBS. Reference 9 describes the discrimination of > 97% of pens and 100% of paper originating from different sources using LA-ICP-MS. Reference 6 reports these laser sampling methods resulting in discrimination of different sources with LIBS producing 89% discrimination and LA-ICP-MS producing up to 100% discrimination (with <5% false exclusion rate for the same samples) while SEM-EDS discriminates less than 50% of the inkjet and toner samples under study [6]. Reference 1 reports that major, minor and trace elements present in ink samples can serve as good discriminators for both toner and inkjet printing inks. In this study, Lithium was found only in inkjet samples and the application of LIBS overcomes the spectral interferences of ICP-MS for the elements K, Ca, Si and Fe, which are good discriminators for both inkjets and toners. The use of LA-ICP-MS and LIBS in “tandem” mode, that is, simultaneously, further improves the discrimination of very similar ink samples. Table 4 summarizes the discrimination of specially selected (similar) toner and inkjet samples using LA-ICP-MS, LIBS and both techniques in tandem by fusing the data from both methods [1].

Table 2: Discrimination of selected printing inks by two methods using spectral overlay (from [1]).

Toner Samples	LIBS	LA-ICP-MS	Tandem (fusion of) LIBS / LA-ICP-MS
# Samples	9 (36 comparison pairs)	9 (36 comparison pairs)	9 (36 comparison pairs)
% Discrimination	100%	66.60%	100%
	(36 out of 36)	(24 out of 36)	(36 out of 36)
Inkjet samples	LIBS	LA-ICP-MS	Tandem (fusion of) LIBS / LA-ICP-MS
# Samples	10 (45 comparison pairs)	10 (45 comparison pairs)	10 (45 comparison pairs)
% Discrimination	97.80%	91.10%	100%
	(44 out of 45)	(41 out of 45)	(45 out of 45)

Elemental Analysis of Soils

Elemental analysis of soil is a useful application of both laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS) in geological, agricultural, environmental, archaeological, planetary, and forensic sciences. In forensic science, the question to be answered is often whether soil specimens found on objects (e.g., shoes, tires, or tools) originated from the crime scene or other locations of interest. Elemental analysis of the soil from the object and the locations of interest results in a characteristic elemental profile of each specimen, consisting of the amount of each element present. Because multiple elements are measured, multivariate statistics can be used to compare the elemental profiles in order to determine whether the specimen from the object is similar to one of the locations of interest. Previous work [7] involved milling and pressing 0.5 g of soil into pellets before analysis using LA-ICP-MS and LIBS. However, forensic examiners prefer techniques that require smaller samples, are less time-consuming and are less destructive, allowing for future analysis by other techniques. An alternative sample introduction method was developed to meet these needs while still providing quantitative results suitable for multivariate comparisons. The tape-mounting method involved deposition of a thin layer of soil onto double-sided adhesive tape [2]. A comparison of the tape-mounted and pellet method performance was reported for both LA-ICP-MS and LIBS [2]. Calibration

standards and reference materials, prepared using the tape method, were analyzed by LA-ICP-MS and LIBS. As with the pellet method, linear calibration curves were achieved with the tape method, as well as good precision and low bias. Soil specimens from Miami-Dade County were also prepared by both the pellet and tape methods and analyzed by LA-ICP-MS and LIBS. Principal components analysis (PCA) and linear discriminant analysis (LDA) were applied to the multivariate data. Results from both the tape method and the pellet method were nearly identical, with clear groupings and correct classification rates of > 94 % [2]. To prepare the tape-mounted samples, spiked calibration standards, reference materials, and sieved soil specimens were carefully re-homogenized using a vortex touch mixer. A 19 x 22 mm piece of Scotch removable poster tape #109 (3M, St. Paul, MN, USA) was affixed to a labeled 30 x 22 mm glass cover slip (Fisher Scientific, Pittsburg, PA, USA), leaving the tape liner on. The liner was folded back halfway to expose an area of adhesive approximately 19 x 10 mm (see figure 3a). A small amount of each specimen (approximately 10 mg) was deposited onto the exposed tape and shaken gently to distribute it evenly (see figure 3b). The deposited sample was smeared and pressed gently to improve adhesion, and then tapped lightly to remove any excess that was not adhered. The liner was folded back down to act as a cover to prevent contamination or loss and was taped in place (see figure 3c). Each tape-mounted specimen was packaged carefully in weighing paper, and labeled (see figure 3d).

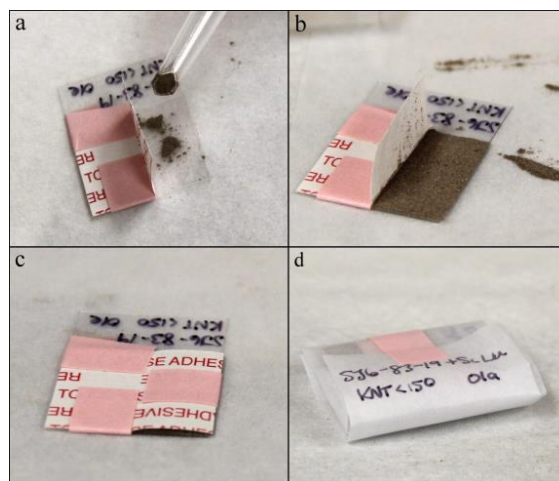


Figure 3. Sample preparation method using tape mounting of soil onto adhesive tape to facilitate the laser sampling using both LA-ICP-MS and LIBS (from [2]).

LIBS experiments were conducted on both a commercial (Applied Spectra) system and compared to a home-built system using a 266 nm Nd:YAG Tempest laser (New Wave Research, Fremont, CA, USA) with a Mechelle 5000 spectrometer and iStar iCCD camera (Andor Technologies, South Windsor, CT, USA) [2]. Acquisition parameters for both pellets and tape-mounted specimens were as follows: 5 replicate measurements per specimen, 75 pulses accumulated per replicate, 900 mL/min argon delivered to the surface, 100 % laser energy, and 148 J/cm^2 focused 1.4 mm behind the surface. Daily performance was tested using NIST SRMs 1831 (“Soda Lime Sheet Glass (1.2 % Al_2O_3)”) and 610 (“Trace Elements in a Glass Matrix (3mm Wafer)”; “Nominal Trace Element Concentrations 500 mg/kg (ppm)”, NIST, Gaithersburg, MD, USA) in air and in argon. For pellets, spot mode was used with three cleaning pulses applied to the each location before beginning each replicate measurement. For tape-mounted specimens, line mode was used, in which the sample stage was moved at a speed of $250 \text{ }\mu\text{m/s}$. Background subtraction was performed by subtracting the intensity at a neighboring blank (background) region of the spectrum from the intensity of the peak. Normalization was performed by dividing the background-subtracted intensity of the each peak by that of the Sc 361.4 nm emission line. Further details can be found in reference 7. Calibration curves were generated from the calibration standards for each emission line, and linear regression was used to calculate the concentrations for all samples. Limits of detection (LODs) were calculated as 3 times the standard deviation of the noise in the background regions of the spectrum. Emission lines monitored included: Ba II 493.4, Ba II 614.2, Ca I 393.4, Ca II 396.9, Ca I 643.9, Cr I 360.5, Cr I 425.4, Cu I 324.8, Fe I 360.9, Fe I 495.8, Li I 610.4, Li I 670.8, Mg I 517.3, Mg I 518.4, Pb I 405.8, Sr II 407.8, Sr II 421.6, Ti I 336.1, V I 437.9, and Zr I 468.8 nm. Figure 4 (left) presents example calibration curves for LIBS analysis of the tape-mounted soil samples using Sc as an internal standard. These results (including precision and LODs) correspond very well with the equivalent pelletized samples. Figure 4 (right) presents a comparison of pellet samples with tape-mounted samples using a PCA plot to visualize the separation between different soil samples incorporating the element menu report above for LIBS analysis.

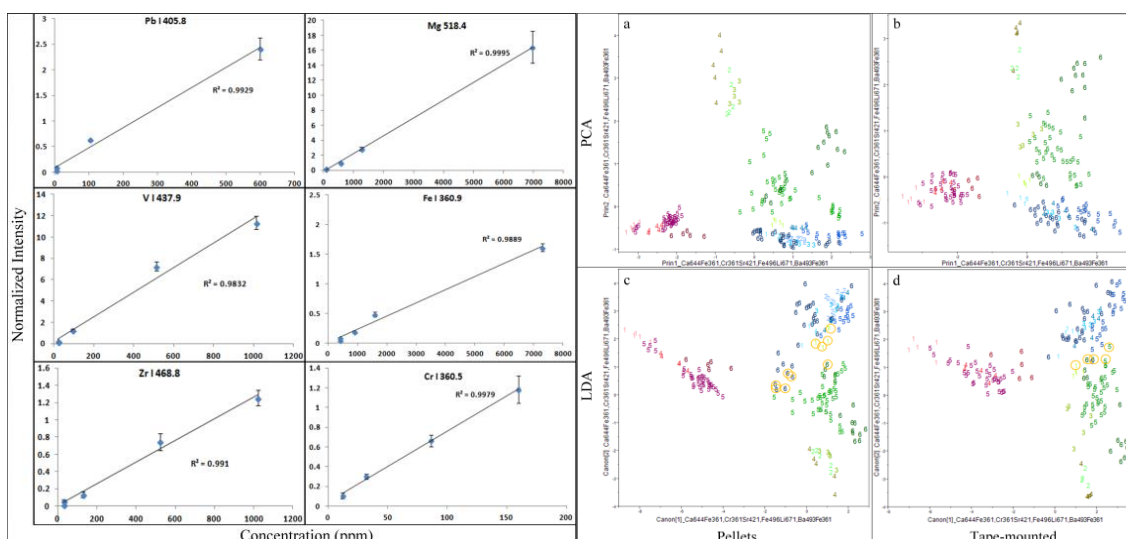


Figure 4. (Left) Example calibration curves obtained from LIBS analysis of spiked, non-milled, tape-mounted calibration standards. Error bars represent one standard deviation. **(Right)** PCA and LDA plots for samples HA (red), KNT (green), and CC6 (blue) generated from LIBS data of sieved pellets and tape-mounted soil. The following discrimination element menu was used: Ca I 643.9/ Fe I 360.9, Cr I 360.5/ Sr II 421.6, Fe I 495.8/ Li I 670.8, and Ba II 493.4/ Fe I 360.9. Numbers and different shades denote the different sub-plots within an area. a. PCA score plot for pellets, b. PCA score plot for tape-mounted specimens, c. LDA canonical plot for pellets, d. LDA canonical plot for tape-mounted specimens. Misclassified specimens are circled (from [2]).

Implications for criminal justice policy and practice

This project included the participation of 4 graduate students at Florida International University and 2 experienced practicing forensic scientists (in Virginia and in Colorado) as collaborators. The greater impact to the forensic science community is the availability of a rapid, simple and relatively inexpensive analytical method that can provide elemental analysis for matrices of importance to forensic scientists. There are currently ~ 140 forensic laboratories in the US with active trace evidence sections and, to date, 15 labs have acquired LA-ICP-MS or LIBS instruments. This research expands the use of these methods beyond the previously reported glass analysis method (ASTM E2926-13) [65].

Conclusions

A total of 10 peer-reviewed publications and more than 50 oral and poster presentations describe the efforts completed through this NIJ award over the last 4 years. LA-ICP-MS and LIBS have both been shown as useful analytical tools for the analysis of paper, inks, soil and cotton. The results have been presented in analytical chemistry and forensic science journals and venues.

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