Evaluation of Laser-Induced Breakdown Spectroscopy (LIBS) for the Elemental Profiling of Forensic Evidence

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is an emerging atomic emission based solid sampling technique that has many potential forensic applications. The work presented in this dissertation was aimed at evaluating a range of elemental profiling methods for forensic applications, with a particular focus on LIBS to determine whether this emerging technique can be readily applied to various forms of forensic evidence. In this study, the analytical performance of a commercially available LIBS instrument was evaluated for the elemental profiling of glass, paper, writing ink, inkjet ink, toner, and Cannabis plant material. Different reference standard matrices, which have similar compositions to the selected sample types, were used to calibrate, develop and optimise the analytical methods, taking into consideration accuracy, limits of detection and precision.

Firstly, the LIBS instrument was evaluated for the determination of elemental composition of twenty window glass samples including 14 laminated samples and 6 non-laminated or non-specified samples collected from crime scenes in the Canberra region, Australia. Three standard reference materials (NIST 610, 612, and 1831) were used to assess LIBS figures of merit. The discrimination potential of LIBS for the analysis of architectural window glass samples was compared to that obtained using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), X-ray microfluorescence spectroscopy (µXRF), and scanning electron microscopy energy dispersive X-ray spectrometry (SEM-EDX). The results showed that, based on the sample set chosen, the elemental analysis of window glass by LIBS provides a discrimination power greater than 97% (> 98% when combined with refractive index data), which was comparable to the discrimination powers obtained by LA-ICP-MS and µXRF.

Document examination is an important forensic discipline, and the legal system regularly needs the knowledge and skills of the scientific expert when questioned documents are involved in criminal or civil matters. Therefore, the evaluation of the analytical performance of LIBS was also conducted on office papers, writing inks, inkjet inks and laser printer toners, which are commonly encountered in forensic casework. The paper sample set analysed in the current thesis consisted of 32 Australian paper specimens originating from the same plant/mill but representing different brands and/or batches. In addition, a total of 131 ink or toner samples were examined that included black and blue ballpoint inks, black inkjet inks, and black laser printer toners originating from several manufacturing sources, models and/or batches. Results
from the LIBS method were then compared against those obtained using more established elemental profiling methods such as LA-ICP-MS and μXRF. LIBS demonstrated detectable and significant differences between different batches of the same brand as well as between different brands of paper, ink and toner samples; and provided comparable discrimination powers for the selected sample sets when compared to those obtained using LA-ICP-MS and μXRF (discrimination of ~ 98.4 – 99.8%, depending on the sample subset under examination).

Finally, the analytical performance of LIBS, as well as that of ICP-MS, LA-ICP-MS and μXRF, was evaluated for the ability to conduct elemental analyses on Cannabis plant material, with a specific investigation of the possible links between hydroponic nutrients and elemental profiles from associated plant material. No such study has been previously published in the literature. Good correlation among the four techniques was observed when the concentrations or peak areas of the elements of interest were monitored. The study demonstrated that ICP-MS, LA-ICP-MS and LIBS are suitable techniques for the comparison of Cannabis samples from different sources, with high discriminating powers being achieved. In addition, for Cannabis samples collected at the same growth time, the elemental profiles could be related to the use of particular commercial nutrients.

Different methods of data analysis were performed over the source of this study in order to investigate relative discrimination powers. The data analysis approach employed was first directed at identifying a set of emission lines, elements and/or isotopes, depending on the applied analytical method and the sample type, and then constructing a set of elemental ratios. The comparison of selected elemental ratios was performed by utilizing a 2- or 3-sigma match criterion (mean value ± 2 or 3 times the standard deviation). Principle component analysis (PCA) was then employed as a second layer of discrimination, in an attempt to reduce the number of variables and to cluster samples into groups. Finally, an analysis of variance (ANOVA) and Tukey’s honestly significant difference (HSD) post hoc test at a 95% confidence limit was employed for the remaining indistinguishable pairs.

Overall, it was demonstrated that LIBS is an excellent tool for the elemental profiling of matrices such as glass, paper, writing ink, inkjet ink, laser toners and Cannabis plant material. LIBS displayed good sensitivity and reproducibility. When combined with ease of use, fast analysis times, and low cost, the findings support the incorporation of the LIBS technique into operational forensic laboratories for the elemental analysis of a range of different evidence types.
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### Abbreviations

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<th>Description</th>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>ACTGAL</td>
<td>The ACT Government Analytical Laboratory</td>
</tr>
<tr>
<td>AES</td>
<td>Atomic emission spectroscopy</td>
</tr>
<tr>
<td>AFP</td>
<td>The Australian Federal Police</td>
</tr>
<tr>
<td>ANOVA</td>
<td>The analysis of variance</td>
</tr>
<tr>
<td>ANU</td>
<td>The Australian National University</td>
</tr>
<tr>
<td>ASAP</td>
<td>An Automated Standardless Analysis Protocol</td>
</tr>
<tr>
<td>ASTM</td>
<td>The American Society of Testing and Materials</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>CBN</td>
<td>Cannabinol</td>
</tr>
<tr>
<td>CE</td>
<td>Capillary electrophoresis</td>
</tr>
<tr>
<td>CIJ</td>
<td>Continuous inkjet</td>
</tr>
<tr>
<td>CL</td>
<td>Confidence limit</td>
</tr>
<tr>
<td>DOD</td>
<td>Drop-on-demand</td>
</tr>
<tr>
<td>DP</td>
<td>Discrimination power</td>
</tr>
<tr>
<td>DRC-ICP-MS</td>
<td>Dynamic reaction cell inductively coupled plasma mass spectroscopy</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>EAWG</td>
<td>The Elemental Analysis Working Group</td>
</tr>
<tr>
<td>EC-ICP-MS</td>
<td>External calibration inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>EDX-XRF</td>
<td>Energy dispersive X-ray fluorescence spectroscopy</td>
</tr>
<tr>
<td>FAAS</td>
<td>Flame atomic absorption spectroscopy</td>
</tr>
<tr>
<td>FDE</td>
<td>Forensic document examiner</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC-FID</td>
<td>Gas chromatography-flame ionization detection</td>
</tr>
<tr>
<td>GF-AAS</td>
<td>Graphite furnace atomic absorption spectroscopy</td>
</tr>
<tr>
<td>GLM</td>
<td>General Linear Model</td>
</tr>
<tr>
<td>GRIM</td>
<td>Glass Refractive Index Measurement</td>
</tr>
<tr>
<td>GW</td>
<td>Ground wood</td>
</tr>
<tr>
<td>HA</td>
<td>The alternate hypothesis</td>
</tr>
<tr>
<td>Ho</td>
<td>The null hypothesis</td>
</tr>
<tr>
<td>HP</td>
<td>Hewlett-Packard</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>HR-SF-ICP-MS</td>
<td>High resolution sector field inductively coupled plasma mass spectroscopy</td>
</tr>
<tr>
<td>HSD</td>
<td>Honestly significant difference</td>
</tr>
</tbody>
</table>
IMS  Ion mobility spectrometer
IRE  An internal reflectance element
IRMS  Stable isotope ratio mass spectrometry
LA-ICP-MS  Laser ablation inductively coupled plasma mass spectrometry
LA-ICP-OES  Laser ablation inductively coupled plasma optical emission spectrometry
LDA  Linear discriminant analysis
LDI-TOF-MS  Laser desorption ionization-time-of-flight secondary ion mass spectrometry
LIBS  Laser-induced breakdown spectroscopy
LODS  Limits of detection
MDLs  The method detection limits
m/z  Mass-to-charge
NAA  Neutron activation analysis
Nd:YAG  Neodymium-doped yttrium aluminium garnet
NIST  The National Institute of Standards and Technology
OES  Optical emission spectroscopy
PCA  Principle component analysis
PFA  polytetrafluoroacetae
PIGE  Particle induced gamma X-ray Emission
PIXE  Particle-induced X-ray emission
ppb  Parts-per-billion
ppm  Parts-per-million
Py-GC-MS  Pyrolysis-gas-chromatography coupled with mass spectrometry
R²  Correlation coefficient
RA  Reflection-absorption
RI  Refractive index
RSD  Relative standard deviation
SD  Standard deviation
SEM-EDX  Scanning electron microscopy with energy-dispersive X-ray microanalysis
STR  Short tandem repeat
SRMs  Standard reference materials
SR-XRF  Synchrotron radiation X-ray fluorescence spectrometry
TAPPI  The Technical Association of the Pulp and Paper Industry
THC  Delta-9-tetrahydrocannabinol
TLC  Thin-layer chromatography
TMP  Thermo-mechanical pulp
TOF-SIMS  Time-of-flight secondary ion mass spectrometry
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TXRF</td>
<td>Total reflection X-ray fluorescence</td>
</tr>
<tr>
<td>UNODC</td>
<td>The United Nations Office on Drugs and Crime</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>WDX-EPMA</td>
<td>Wavelength-dispersive electron probe microanalysis</td>
</tr>
<tr>
<td>WDX-XRF</td>
<td>Wavelength-dispersive X-ray fluorescence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>μXRF</td>
<td>Energy dispersive micro-X-ray fluorescence spectrometry</td>
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