J22 Forensic Analysis of Inks by Laser Induced Breakdown Spectrometry (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

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The goal of this presentation is to provide the forensic community with a critical evaluation of the value of using LIBS and LA-ICP-MS for the elemental profiling of writing inks.

This presentation will impact the forensic science community by proposing innovative methods for the forensic examination of writing inks. Advantages and limitations of the use of LIBS and LA-ICP-MS on ballpoint and non-ballpoint inks will be also presented.

Document related crimes are considered a very prevalent form of crime that has a serious economic impact on society. The physical and chemical examination of writing inks has been the focus of many criminal investigations and in routine document examinations, non- destructive analytical methods such as microscopic and optical techniques are applied first. However, these methods are often unable to sufficiently characterize the inks used to prepare the document or to determine attribution between a questioned ink samples to a known source. Moreover, 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

writing inks to assist document examiners to overcome analytical challenges that otherwise are difficult to address using conventional methods of analysis. The purpose of the present work is to conduct method development and evaluation of the capabilities of two alternative techniques, LIBS and LA-ICP-MS, for the elemental analysis and comparison of writing inks. Laser sampling (LIBS and LA-ICP-MS) can provide good spatial resolution for the direct removal and subsequent elemental analysis of very small samples on surfaces such as ink deposited on a paper substrate. Some of the recognized advantages of LA-ICP-MS include direct characterization of solids, elimination for the need for chemical procedures for dissolution, minimum consumption of the sample (~nanograms), high sensitivity and high selectivity. Although less mature than LA-ICP-MS, LIBS also shares the benefits associated to laser ablation methods with the added advantage of improved speed, versatility, ease of operation and data interpretation, affordability and portability. An evaluation of the parameters of forensic interest will be investigated in detail including the comparison of the analytical performance of each technique, the homogeneity of the inks at the micro- scale, sampling size requirements, data analysis and interpretation of the results. Another key objective of this presentation consists in the evaluation of the meaning and value of the elemental composition in the discrimination and comparison of writing inks. Sample collections representing ballpoint inks and non-ballpoint inks originating from a known variety of sources will be used to evaluate the discrimination capabilities of the LA-ICP-MS and LIBS methods and to determine type I and type II error rates. The sample sets used for the discrimination studies consist of black gel ink collected from 24 different sources, blue gel ink collected from 22 different sources and black ballpoint ink collected from 18 different sources. The variability of the elemental composition of inks was also studied within ink samples collected from pens originating from the same package. The results show that both the LIBS and LA-ICP-MS methods provide good discrimination between the different inks with very low type I and type II errors and therefore can be useful for the comparison and classification of writing inks and could potentially be optimized for the analysis and identification of other type of inks such as from inkjet printers. The proposed methods can facilitate the chemical analysis of questioned documents by incorporating LIBS and LA-ICP-MS within the analytical strategy. **Inks, Trace Elemental Analysis, LIBS**

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