A73 Evaluation of Capabilities of Laser Ablation ICP-MS for the Forensic Analysis of Gel Pen Inks

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

This presntation will impact the forensic community by proposing an innovative method for the forensic examination of gel inks. The use of LA-ICP-MS on inks will also expand the number of matrices currently analyzed by this technique in trace evidence and will facilitate the use of this methods in forensic laboratories.

Gel pen inks have become a prominent type of ink found in forensic document examinations due to its favorable chemical and physical characteristics 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 Ramman spectrometry, infrared spectroscopy and XRF have been recently explored as alternative tools to cope with forensic comparisons of gel inks.

The purpose of the present work is to conduct method development and evaluation of the capabilities of LA-ICP-MS for the qualitative and quantitative elemental analysis and comparison of gel inks.

Laser ablation is a leading technology for direct solid sampling and has become a valuable tool for elemental analysis in forensic science. The technique has been successfully used for forensic analysis of glass, paints, soils, diamonds, gold and other matrices. Some of the 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.

These advantages make LA-ICP-MS a very attractive technique for forensic analysis, especially for ink examinations where the amount of sample always represents a challenge and quasi non-destructive methods are important.

A comprehensive evaluation of the capabilities and limitations of this novel technique are presented in this work. Evaluation of parameters of forensic interest is discussed in detail, including the analytical performance of the technique, accuracy, precision, discrimination potential, homogeneity of the ink and the paper at micro-scale, reproducibility, sampling size requirements, data analysis and interpretation of results.

Laser ablation was optimized in low density energy mode in order to minimize the destruction of ink and its supporting media. Qualitative determinations were conducted on a set of 45 black gel inks in order to evaluate its discrimination power and to identify the most informative elements. Quantitative analysis of the samples was also conducted by LA-ICP-MS to better characterize the elemental profile of the unknowns.

In-house matrix match standards were designed to conduct quantitative determinations. Different papers (Whatman 2, 42 and 542) were tested as the support matrix for the preparation of the ink standards. Fountain pen black ink was spiked with a large suite of elements and analyzed by acid digestion ICP-MS and LA-ICP-MS. Excellent correlation was obtained between the concentration of the ink obtained by acid digestions and LA-ICP-MS.

External calibration and standard addition methods were used to characterize the ink standards. Good accuracy and precision were obtained at different spike levels (%bias <13%, %RSD <5%). Good linearity was achieved for the standard calibration curves where the amount of ablated ink ranges between 0.8-8 pg.

Scanning Electron Microscope images and elemental analysis by SEM/EDS and XRF were used to assist the method development and characterization of the ink standards.

A study on different papers commonly found in forensic document examinations was also conducted to further evaluate the applicability of the method to real case scenarios. The proposed method could be potentially extended to other type of writing inks to enhance discrimination and classification of inks.

Inks, Trace Elemental Analysis, Laser Ablation

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