



A110 Elemental Analysis and Comparison of Bulk Soil Using LA-ICP-MS, μ XRF, and LIBS Methods: An Inter-laboratory Study

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After attending this presentation, attendees will better understand the use of elemental analysis methods for the analysis of bulk soil samples. Elemental analysis of soils has many applications in the environmental, forensic, and geological sciences. The provenance or origin of soil transferred to objects such as shoes or tires can be useful in a criminal investigation and elemental profiles can be used to discriminate soil samples originating from different geographic regions and also associate soil samples originating from the same source.

This presentation will impact the forensic science community by comparing standardized and validated elemental analysis methods for bulk soil analysis. Thirteen laboratories have participated in a round robin exercise, and the results will be presented here.

Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), micro X-ray fluorescence (μ XRF), and laser-induced breakdown spectroscopy (LIBS) were used in this study since all three techniques produce similar analytical figures of merit. LA-ICP-MS and μ XRF methods are established elemental analysis instrumental techniques that are currently available in many forensic laboratories. A LA-ICP-MS method was recently optimized for analysis and comparison between different soil samples in an environmental forensic application^{1,2} and LIBS produces sensitivity equal to or better than that of μ XRF (especially in the low mass range). LIBS has recently attracted the interest of analytical chemists and forensic laboratories as a simpler, lower cost alternative to the more established analytical methods. In developing a LIBS method, there are many parameters to consider, including laser wavelength, spectral resolution, sensitivity, and matrix effects. The first LIBS method using a 266 nm laser for forensic soil analysis has been also been reported by our group and presented.³

A soil analysis round-robin test was organized by Florida International University and distributed amongst some of the members of the Elemental Analysis Working Group (EAWG). The aims of this first soil round robin (EAWG-RR5) were: a) to evaluate the inter-laboratory performance of the three methods in terms of accuracy (bias), precision (relative standard deviation, RSD) and sensitivity using standard reference materials (SRMs); b) to evaluate the newly released NIST SRM 2710a, which supersedes 2710; and c) to evaluate the utility of LIBS as an alternative technique to LA-ICP-MS and μ XRF for bulk analysis of soils.

Samples were submitted to thirteen laboratories: six used LA-ICP-MS, five used XRF and two used LIBS. Four samples were sent to each laboratory for analysis, consisting of standard reference materials: NIST SRM 2704 Buffalo River Sediment, NIST SRM 2710 Montana I Soil, NIST SRM 2710a Montana I Soil, and NRC Canada PACS-2 Marine Sediment Reference Material. For LA-ICP-MS, one of the samples was used as the single-point calibrator. For μ XRF and LIBS, participants were asked to construct a calibration curve from four additional samples with known concentrations of the elements of interest. Each sample and standard was homogenized in a high-speed ball mill and pressed into pellets. Participants were instructed to measure the following elements: ⁷Li, ²⁵Mg, ²⁷Al, ⁴²Ca, ⁴⁵Sc, ^{47,49}Ti, ⁵¹V, ⁵⁵Mn, ⁸⁸Sr, ¹³⁷Ba, ^{206,207,208}Pb (LA-ICP-MS); Ti, Cr, Mn, Fe, Cu, Sr, Zr, Pb (μ XRF); Ba, Cr, Cu, Fe, Li, Mg, Mn, Pb, Sr, Ti, Zr (LIBS). For both LIBS and μ XRF, the choice of appropriate spectral lines was determined by the user, optimizing for linearity, sensitivity, and precision.

Results for both LA-ICP-MS and μ XRF were generally consistent for most elements, resulting in good intra-laboratory precision (< 8 % RSD for LA-ICP-MS; < 20 % RSD for μ XRF) and low bias (< 10% for LA-ICP-MS; < 35 % for μ XRF), which are important characteristics for forensic comparison of soils. Linear calibration curves were also obtained for both μ XRF and LIBS. Results for LIBS showed good precision (< 15 %) and bias (< 15 %) for most elements. Some problem elements have been identified and are discussed. Limits of detection for trace and minor elements were in the 0.01 – 1 ppm range for LA-ICP-MS and 1 to 200 ppm for LIBS.

Unlike some other matrices such as glass, soil can be spiked with internal standard(s) and calibration standards can be easily created, allowing for quantitative analysis using an external calibration curve. The result of this first soil round robin study bodes well for future method development in the characterization and forensic analysis/comparison of bulk soil composition.

References:

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2. L Arroyo, T Trejos, T Hosick, S Machemer, JR. Almirall, and PR Gardinali, Analysis of Soils and Sediments by Laser Ablation ICP- MS: An Innovative Tool for Environmental Forensics, *J. of Environmental Forensics*, 2010, 11(4), 315-327.



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Soil, Elemental Analysis, LA-ICP-MS, uXRF, LIBS