A109 Soil Discrimination and Provenancing by Laser Induced Breakdown Spectroscopy (LIBS) as Compared to Other Elemental Analysis Methods

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After attending this presentation, attendees will understand how the application of Laser-Induced Breakdown Spectroscopy (LIBS) for the elemental analysis of soil can provide for the discrimination and/or association of soil samples. Attendees will also learn the advantages of LIBS over other analytical methods.

This presentation will impact the forensic science community by introducing a strategy for the differentiation of soils incorporating LIBS as an analytical tool for elemental analysis. The presentation will also compare the LIBS results to other more accepted analytical techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA- ICP-MS), and micro X-Ray Fluorescence (µXRF).

The goals of this study were to develop a method for the qualitative and quantitative elemental analysis of soil samples using LIBS and to apply the method to the analysis of environmental soil sample sets for discrimination and provenancing. Soil contains a mixture of mineral, organic and anthropogenic material, which varies greatly from region to region, resulting in a large variation of the major, minor, and trace components. The elemental profile can be used to discriminate soil samples originating from different geographic regions and associate samples originating from the same source. For example, the provenance of soil transferred to objects such as shoes, tires, or instruments would provide valuable information in a criminal investigation. In addition to the discrimination of soil samples themselves, an optimized soil analysis method could also be used in the future as a tool to examine the effects of soil diagenesis in bone, and possibly in field analysis applications. Many techniques have been used to determine the elemental profile of soil samples, including those mentioned above. LIBS is an emerging technique that provides many advantages over these techniques. For example, LIBS is relatively inexpensive, fast, and easy to use. Additionally, field-portable instruments have recently become available. The LIBS spectrum provides a richness of information on all the elements present without the requirement for prior knowledge of the element menu. In addition, LIBS has good sensitivity in the low atomic mass range, which is often an issue for both LA-ICP-MS and µXRF. For the LIBS analysis, a pulsed Nd:YAG laser is used as the excitation source to create a very small plasma. The light emitted from the plasma is focused into a high resolution Mechelle spectrometer coupled to an intensified CCD camera detector. The emission lines collected are characteristic of the elemental composition of the sample. The initial sample set includes ten contaminated soil samples, taken at various locations and distances around an automotive battery manufacturing facility. These samples were initially analyzed for environmental contaminants (lead, tin, and antimony) using ICP-MS and also by ICP-OES.[1] These results are now compared to the results obtained using LIBS, as well as LA-ICP-MS and µXRF. A second, larger, sample set taken from a broader geographical area is used to further test the method. Two soil standard reference materials were used for method optimization and as control standards during the elemental analysis of the samples. The element menu was chosen to maximize precision, signal to background ratio, and linearity of response. All samples, blanks, and standard reference materials were spiked with internal standards, homogenized using a high speed ball mill mixer, and pressed into pellets without the need for the addition of a binder. An external calibration curve was constructed using blank sand spiked with various levels of the elements of interest. A convenient ratio comparison tool has been developed by the Almirall group that facilitates the forensic comparison of soils. Discrimination was performed using multivariate statistical analysis, such as pairwise comparison by analysis of variance (ANOVA) and correlation/discrimination trends are also reported using principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). An analytical method was successfully developed for the elemental analysis of soil by LIBS. Good correlation was observed between the different methods making LIBS a viable alternative to the more expensive and complicated techniques.

Reference:

[1] Arroyo, L., Trejos, T., Gardinali, P.R., Almirall, J.R., *Spectrochim. Acta Part B* 64 (2009) 16-25.

Soil, Elemental Analysis, Discrimination

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