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Improved Analytical Characterization of Solid Waste-Forms by Fundamental Development of Laser Ablation Technology

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Research Objective

This EMSP research endeavors to understand fundamental laser-ablation sampling processes and to determine the influence of these processes on analytical characterization of EM waste-site samples. The issues germane to the EMSP are sensitivity and accuracy of analysis. These issues are researched by studying fractionation, sample transport, mass loading, and analytical system optimization. Inductively coupled plasma - mass spectroscopy (ICP-MS) is emphasized in this research because of its use throughout the DOE labs and sites.

Research Progress and Implications

This report summarizes research performed over the first half of this three-year program. Four issues were emphasized to improve analytical sensitivity and accuracy, including the time dependent laser removal of mass from a solid sample, fractionation, particle generation and transport, and optimization of the ICP-MS for laser ablation sampling. This research has led to six journal publications.

One of the first issues addressed was that of accuracy of chemical characterization from mixed-component samples. We identified two primary parameters that effect accuracy, mass loading in the ICP and fractionation (preferential removal of elements based on vapor pressure) (1). When the laser beam ablates the sample, a significant portion of mass is transported to the ICP. If the temperature or electron number density in the ICP is perturbed by this mass, accuracy will be compromised. We investigated mass loading by ablating samples using a wide range of laser properties (2). The temperature of the ICP was measured using a ratio of Fe emission lines, and the electron number density was measured using a ratio of Mg ion to emission lines. Using a nanosecond-pulsed Nd:YAG laser, which is similar to those used in the commercial laser ablation attachments, we identified laser power densities in which mass loading was not significant for a number of samples. However, there were samples in which these same power densities did cause mass loading, such as glasses and soils. Further studies of ICP and laser conditions need to be completed for these samples.

Fractionation (mass removal based on thermal properties) continues to be one of the most difficult problems effecting accuracy of laser ablation sampling. In this research, we investigated the effect of fractionation for two different cases, fractionation as a function of elemental composition in a suite of alloys (3) and as a function of time (4). The number of laser pulses at a fixed location on the sample and the laser power density were found to have a significant influence on fractionation. We found that it is almost impossible to completely eliminate fractionation from many samples, including alloys, ceramics, glasses, and other refractory materials. The extent of fractionation depends on the concentration of the volatile elements; the lower the concentration, the greater the degree of fractionation (3). Even though fractionation exists, it is possible to use solid standards to calibrate the ICP, assuming that fractionation from the standards is similar to that in the sample. ICP-MS data for a suite of elements versus concentration showed a linear relationship with good correlation by using NIST and three other glass samples. However, standards are not likely to be available for waste-site samples; studies will continue in order to better understand and eliminate fractionation for these samples.

Analytical sensitivity was addressed by studying ways to enhance the laser ablation efficiency and by optimizing the ICP-MS system for dry sample introduction. Optimization of sample-gas

flow rate, ICP power, and ICP-MS lens voltages was performed. We demonstrated that the sensitivity could be enhanced by over an order of magnitude by optimizing these parameters, for the dry sample vapor characteristic of laser ablation. The reduction of space charge in the MS is thought to be responsible for the increased sensitivity when the ICP was optimized. The use of different noble gases in the ablation chamber also was found to enhance sensitivity. The enhancement was found to be dependent on the laser's pulse duration. For the nanosecond-pulsed laser, helium and neon provided an increased mass ablation efficiency. For picosecond laser ablation sampling, only helium provided an enhancement (5,6). We demonstrated enhanced sensitivity by almost three orders of magnitude by using picosecond UV compared to nanosecond IR laser ablation, and helium gas. The enhanced sensitivity is beneficial for detecting trace contaminants in EM waste-site samples.

References

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Planned Activities

The general thrust of understanding laser ablation sampling and improving analytical capabilities will continue. Immediate plans are to write a seventh manuscript describing the optimization of the ICP-MS system for laser ablation sampling. We will continue to study the effects of fractionation. A primary quest will be to determine where fractionation occurs; is it occurring at the ablation site during the laser pulse, during the plasma-sample interaction, during particle nucleation and/or particle transport, or in the ICP itself. Another area that will be investigated is particle generation and transport, and sample chamber design. For liquid samples, extensive studies have been carried out on the design of nebulization chambers for accurate and sensitive chemical analysis. Laser ablation sample chambers and dry-vapor transport studies are preliminary, and not conclusive in defining general parameters for chemical analysis. Entrainment of ablated mass into the gas and transport to the ICP is particle size dependent. Transport efficiency needs to be accurately determined as a function of particle-size distribution. The size and composition of the particles may also effect fractionation. Also, we plan to perform the laser ablation sampling studies using samples that are germane to the EMSP mission. Carol Jansen at the Savannah River Site is in the process of sending prototypic waste-glass samples.