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Project Title: **Improved Analytical Characterization of Solid Waste-Forms by Fundamental Development of Laser Ablation Technology**

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

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Introduction

Laser ablation (LA) with inductively coupled plasma mass spectrometry (ICP-MS) has been demonstrated as a viable technology for sample characterization within the EM complex. Laser ablation systems have been set up at the Hanford Site, Savannah River Plant, the Pu immobilization program (MD), Los Alamos, and at numerous other DOE facilities. Advancement of this technology is warranted to guarantee accuracy of analysis for the diversity of complex EM samples. This EMSP research endeavors to understand fundamental laser-ablation and ICP-MS detection characteristics, to ensure accurate and sensitive analytical characterization for EM waste-site samples. The difficulty in characterization of EM waste samples is that matrix-matched standards are not available. ICP-MS instrumental calibration must be performed with a series of standards. The sample-matrix will influence the ablation process, such as an amount of ablated mass, elemental fractionation, particle size distribution and particle transport characteristics, and ICP-MS response. If matrix-matched standards existed, the quantity of mass, degree of fractionation, and particle transport would be the same for standards and samples; hence, accuracy of analysis would be guaranteed. In contrast, for most EM samples in which standards are not available, accuracy can only be accomplished through knowledge of the laser ablation processes.

Research Summary for FY99

The following issues were studied to improve applicability of laser ablation for accurate and sensitive characterization of EM solid samples:

1. Effects of particle size distribution on ICP-MS signal intensity.
2. Effects of sample matrix on dry ICP plasma.
3. ICP-MS optimization for laser ablation sampling.
4. Space charge effects on ICP-MS detection.
5. Importance of matrix matched standards.

Research Progress

1. Effect of particle size distribution on ICP-MS signal intensity.

Problem significance and relevance to the DOE material characterization needs.

The amount of mass removed from the sample per each laser pulse, entrainment of particles in the chamber, transport of particles through the tubing, and atomization and ionization of particles in the ICP all influence the efficiency of the LA-ICP-MS system. Furthermore, entrainment efficiency plays a crucial role in analysis of radioactive materials where chamber and transfer tube contamination should be minimized as much as possible.

Research results.

The relation between laser-generated particles and ICP-MS signal intensity was investigated using single pulse laser ablation sampling of Savannah River Site (Vitrification Facility) prototypical waste-glass samples. The particle size distribution was measured using an optical particle counter for different laser ablation conditions. For single pulse laser ablation, fewer particles were produced for the first pulse than successive pulses that repeatedly irradiated the same surface location. ICP-MS signal intensity corresponding to the first pulse was lower compared to successive pulses. Size distribution of laser-generated particles changed with laser power density and beam diameter. Laser power density of about 0.4 – 0.5 GW/cm^2 was found to be a threshold value, over which particle size distribution changed. Laser beam diameter was the more influential parameter than power density in efficient particle generation. The onset of ICP-MS intensity time profiles decreased as more large particles were generated, indicating particle-size dependent separation within an ablation chamber. ICP-MS intensity data were calibrated with respect to the particle mass entering the torch. Particle entrainment efficiency of the LA-ICP-MS system was found to be a strong function of laser power density (Figure 1). Particle entrainment efficiency decreases from about 25% at low laser power density to less that 5% at high power density. These data demonstrate that at high laser power density, more mass will be lost, leading to contamination of the ablation chamber and particle-transfer tubing.

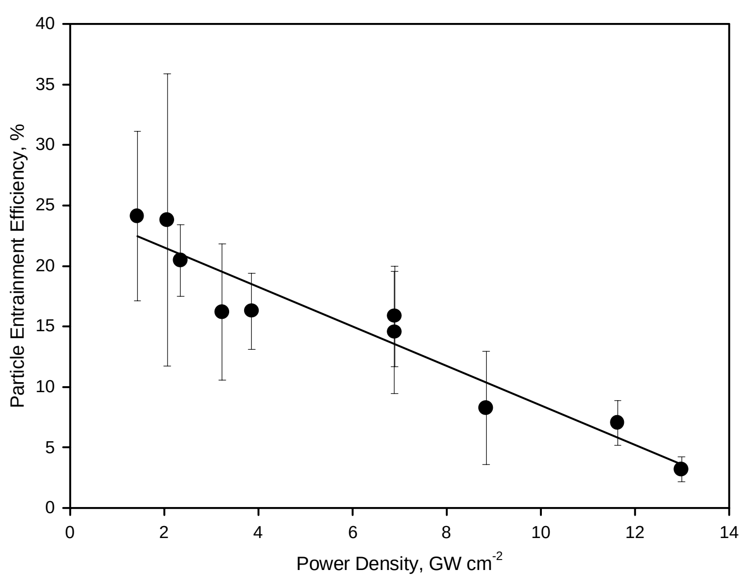

Figure 1. Particle transport efficiency in LA-ICP-MS as a function of laser power density. Laser was operated in a single pulse mode.

2. Matrix effects on dry ICP plasma conditions.

Problem significance and relevance to the DOE material characterization needs.

Analytical performance characteristics of LA-ICP-MS are determined by the ICP operating parameters. Different quantities of mass entering the ICP plasma during laser ablation of samples and standards are not uncommon. For accurate chemical analysis of laser ablated mass with ICP-MS, the ablated mass entering the ICP must not perturb the plasma conditions. Thus, studies of matrix loading in the ICP are an important step in developing LA-ICP-MS for DOE applications.

Research results.

The chemical matrix effect on the plasma conditions was studied by optically measuring the ionic to atomic spectral line intensity ratios in the ICP. The values of these ratios depend on plasma temperature and electron number densities. Electron number densities and plasma temperature are important parameters determining particle vaporization and ionization efficiency. It was found that the matrix effect using laser ablation solid sample introduction and solution nebulization is different, due to the different nature of wet and dry ICP plasmas. Figure 2 illustrates a matrix effect by showing the percentage ratio change of Zn ionic to atomic emission lines in the ICP as a function of a relative matrix amount. Effect of CaF_2, MgO, and Li_2CO_3 matrices are compared. In these experiments, laser ablation was performed in two chambers simultaneously. In the first test chamber, laser ablation of Zn was conducted at constant energy conditions. Laser ablation of matrix was done in the second chamber.

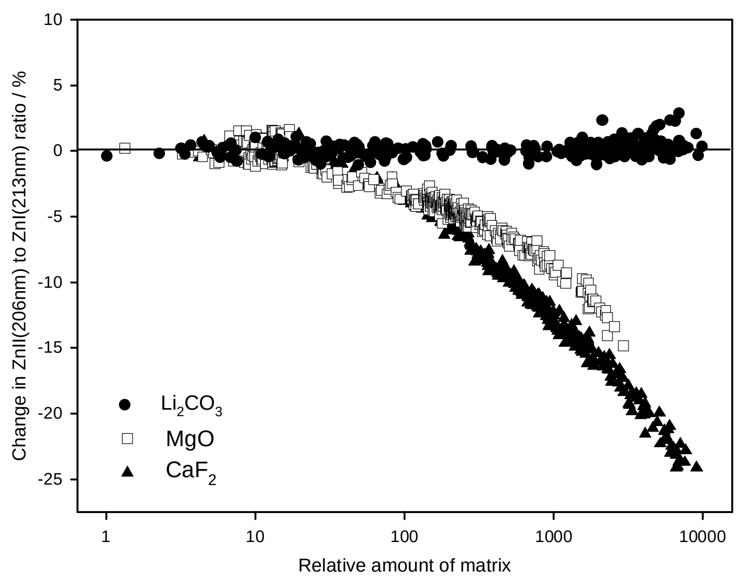

Figure 2. Percentage ratio change of Zn ionic to atomic emission lines in the ICP as a function of a relative amount of CaF_2, MgO, and Li_2CO_3 matrices.

Li_2CO_3 matrix showed no observable change in the plasma conditions while CaF_2 and MgO showed a drastic change in plasma conditions. In general, it was determined that Ca has more pronounced matrix effect on ICP plasma than other easy ionizable elements (such as Li, Na, and K). The chemical composition of the waste-site sample must be preliminary known to ensure accurate analysis. Preliminary knowledge of sample composition also is warranted with solution digestion. Laser ablation still benefits by not having to digest the sample and generate additional waste.

3. ICP-MS optimization for laser ablation sampling.

Problem significance and relevance to the DOE material characterization needs.

ICP-MS optimization will influence sensitivity of analysis. Instrumental parameters for laser ablation and liquid nebulization sample introduction are expected to be different. Fundamental understanding of conditions that govern ICP-MS optimization will allow one to directly analyze solid materials without using liquid standards.

Research results.

ICP-MS optimization was done during steady state laser ablation of various samples, including Zr metal and NIST 610 glass. Ar gas flow rate, that carries ablated particles into the ICP, must be optimized: first, to provide favorable vaporization and ionization conditions in ICP and second, to minimize particle losses inside a chamber and transfer line. Typical Ar gas flow rates used in laser ablation work are in the range of 0.7 – 1.0 L min^{-1}. These flow rates are governed primarily by ICP ionization requirements. Figure 3 shows ICP-MS signal intensity as a function of Ar gas flow rate. Typical dependence was observed when flow rate was varied from 0.1 to 1.4 L min^{-1} (bottom axis). In contrast, when ICP conditions were maintained constant, keeping the total

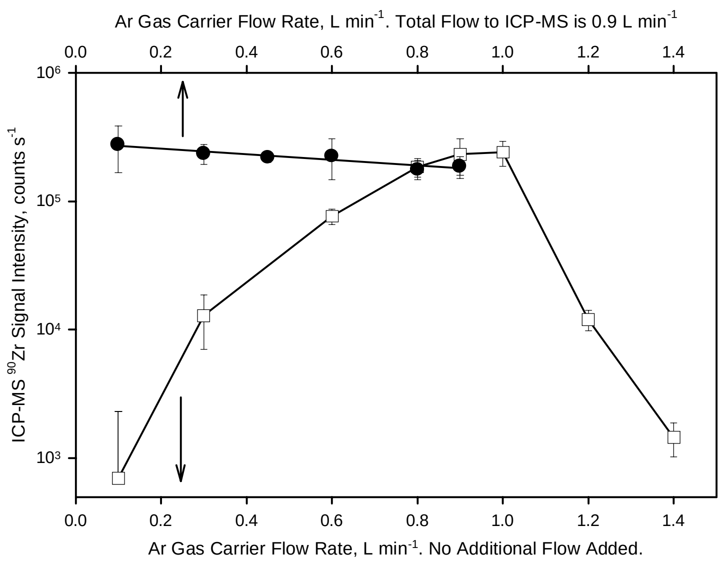

Figure 3. ^{90}Zr ICP-MS signal intensity as a function of a carrier Ar gas flow rate during repetitive ablation of Zr metal with no additional flow (bottom axis) and with various flow rates through the ablation chamber, but fixed total flow rate of 0.9 L min^{-1} into the ICP (top axis).

flow into the ICP the same (by mixing Ar gas flow through the chamber with an additional flow at a base of an ICP torch), ICP-MS signal intensity did not change significantly in the range of carrier flows of 0.1 – 0.9 L min^{-1}. These data demonstrate that central channel flow rates are determined by ICP plasma conditions and not by particle transport properties. Flow rate of 0.1 L min^{-1} is as efficient in transporting ablated mass as much higher 0.9 L min^{-1} flow.

ICP-MS ion-optics optimum voltages were found to be significantly different for dry and wet ICP plasmas. Two orders of magnitude improvement in sensitivity was observed when the ICP-MS was tuned for solid sampling conditions. ICP conditions, such as temperature and electron number density, determine ICP sampling through the interface and, hence, total ion current through the ion optics. Based on optically measured ICP temperature and electron number densities, total current for sampling from dry and wet plasmas was compared. For the typical operating conditions ion current for sampling from wet plasma is only in the range of 0.2 – 1.0 μA, whereas for sampling from dry plasma the current is about 10 μA. This is believed to be determining factor in optimum ion-optics settings. Furthermore, the average ion kinetic energies for the dry plasma is about 5 – 6 eV lower than for the wet plasma.

4. Space charge effects in ICP-MS.

Problem significance and relevance to the DOE material characterization needs.

ICP-MS matrix effects, known as space charge effects, can significantly contribute to analytical uncertainties, especially when light elements have to be determined in a background of a heavy-element matrix. For example, determining alkali and/or alkali-earth elements in Pu or U oxides will cause space charge effects, supressing light-elements response. In this work we qualitatively investigated space charge effects in the ICP-MS and their influence on instrumental operating conditions.

Research results.

The ICP-MS interface was modified using a three-grid ion energy analyzer. This system allows for kinetic energy of sampled ions to be measured. The principle behind such measurements is that ion transmission through an analyzer drops when the applied voltage matches the ion kinetic energy. As a result, stopping curves can be obtained. Figure 4 compares stopping curves for Ba and Li at different Ar gas flow rates. It can be seen that Ba stopping curves are unaffected by Ar gas flow rate. In contrast, Li curves have different shape at different flows. At high flow rates of 1.0 and 1.2 L min^{-1} stopping curves resemble those for Ba. When flow rate was decreased to 0.7 L min^{-1} this behavior changed. As stopping voltage increases, Li signal decreases but at slightly higher grid potentials, indicating some increase in Li kinetic energy as flow was decreased. At grid potential of about 7 – 8 V Li signal intensity sharply increases and tails off as potential increases further. The sharp signal increase becomes more significant as flow rate was further reduced to 0.5 L min^{-1}. It also can be noted that at this Ar gas flow rate, Li ions have higher kinetic energies. As flow rate was reduced to 0.3 L min^{-1}, only backgound Li levels were detected (note that the data presented in Figure 4 were normalized to the highest signal intensity for each curve). At grid potential of about 9 V Li counts increase and then slowly decrease as potential was further increased.

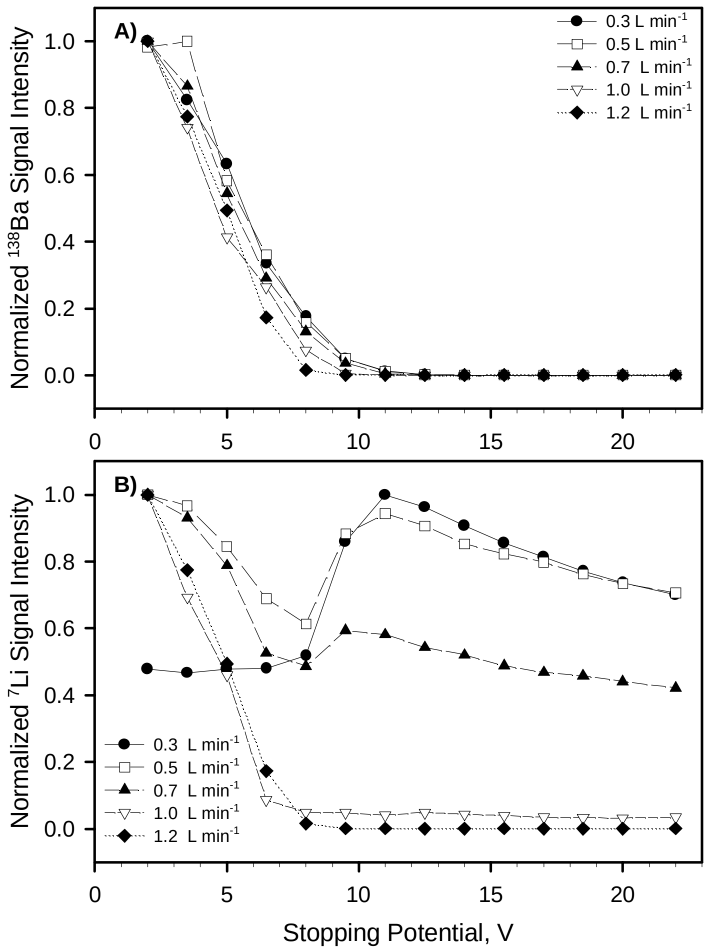

Figure 4. ^{138}Ba (a) and ^{7}Li (b) stopping curves at different flow rates (given in legends).

Space charge effects have more influence on light masses. After the second expansion stage, electro-neutrality of the beam can be lost. Positive potential applied to the extraction lens facilitates this process. As a result of charge separation, ion-ion interactions push highly mobile light elements to the outer regions of the beam, whereas heavy elements stay on axis. Space charge effects are more severe as ion current through the skimmer cone increases. As was determined, ion current depends on plasma operating conditions and decreases from about 200 μA to about 20 nA as flow rate was increased from 0.4 to 1.4 L min^{-1}. This explains anomalies in Li stopping curves. At low flow rates and high ion currents, space charge effects are strong. In contrast, significance of space charge diminishes as flow rate increases (low ion currents). As grid potential increases, the total ion current through the energy analyzer drops. Because light elements are concentrated at the outer zones of the ion beam they can gain energy upon collisions with heavy ions as the later are repealed by the positive potential at the grid. This will allow for light ions to gain enough energy to pass through the energy analyzer.

Conclusion

The research performed for this EMSP project clearly demonstrates that a fundamental understanding of laser ablation and ICP-MS operating conditions can lead to enhanced sensitivity and guarantee accuracy of analysis for characterization applications within the EM program. LA-ICP-MS technology provides significant cost savings for the EM program by eliminating sample digestion procedures, eliminating additional waste, and ensuring safety of personnel. This FY99 EMSP effort clearly demonstrated that the chemical matrix effect is a remaining area that needs to be understood for achieving accurate analysis without matrix-matched standards. Eliminating the need for matrix-matched standards would be a major breakthrough in the use of laser ablation for complex waste-site samples.

PUBLICATIONS RESULTING FROM THIS EMSP AWARD:

Optimization Conditions for ICP/MS Laser-Ablated Mass Sampling: Relevance to Ion Energies, O.V. Borisov, X.L. Mao, and R.E. Russo, ***submitted to Analytical. Chemistry, June 1999***.

Effects of Particle Size Distribution on ICPMS Signal Intensity During Laser Ablation of Glass Samples, S.H. Jeong, J. Yoo, X.L. Mao, and R.E. Russo, ***submitted to Analytical Chemistry, April 1999..***

Laser Ablation ICP/MS calibration based on binary Cu/Zn alloy standards, O.V. Borisov, X.L. Mao, and R.E. Russo, ***accepted in Spectrochimica Acta B, March 1999***.

Influence of Gas Atmosphere on Picosecond Laser Ablation Sampling Efficiency and ICP-AES, A.P.K. Leung, W.T. Chan, X.L. Mao, and R.E. Russo, ***Analytical Chemistry, V70 (N22), 4709 (1998).***

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Time Resolved Parametric Studies of Laser Ablation of Brass Using ICP-AES, X.L. Mao, A.C. Ciocan, O.V. Borisov, and R.E. Russo, ***COLA, July 1997, Asilomar CA.***

Optical Emission Spectroscopy Studies of Ablated Material on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, ***COLA, July 1997, Asilomar CA***.

PRESENTATIONS RESULTING FROM THIS EMSP AWARD:

Fundamental and Applied Aspects of Laser Ablation for Chemical Analysis, Frontiers in Chemistry Lecture Series, Wayne State University, April 1999 **(Invited)**

Particle Generation and Transport During Laser Ablation Sampling for Chemical Analysis, R.E. Russo, S.H. Jeong, X.L. Mao, O.V. Borisov, and J. Yoo, 25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 1998, Austin, TX **(INVITED).**

Optimization of ICPMS for Laser Ablation Sampling, O.V. Borisov, X.L. Mao, and R.E. Russo, 25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 1998, Austin, TX**.**

Laser-Ablation Sampling with ICP/AES and ICP/MS: Fundamental Issues to Improve Analytical Applications, R.E. Russo, *Society of Applied Spectroscopy California Section Meeting, September 1998, Fremont, CA* **(INVITED).**

Laser Ablation Solid Sample Chemical Analysis: Dream or Reality, R.E. Russo, X.L. Mao, A.C. Ciocan, and B.V. Borisov, *Twenty-Fourth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, (FACSS), October 1997, Providence, RI* **(Invited).**

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