FINAL REPORT

U.S. DEPARTMENT OF ENERGY

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

Richard E. Russo, Senior Scientist
Lawrence Berkeley National Laboratory
Mail Stop 70-108B
BERKELEY, CA 94720
(510)-486-4258
rerusso@lbl.gov

Project Number: 55318

Grant No. DEAC-03-76SF00098

Grant Project Officer: Roland Hirsch

Project Duration: September 1996 – October 2000
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cover Sheet</td>
<td>1</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>2</td>
</tr>
<tr>
<td>Executive Summary</td>
<td>3</td>
</tr>
<tr>
<td>Research Objectives</td>
<td>5</td>
</tr>
<tr>
<td>Methods and Results</td>
<td>7</td>
</tr>
<tr>
<td>Mass Loading</td>
<td>7</td>
</tr>
<tr>
<td>Fractionation</td>
<td>8</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>8</td>
</tr>
<tr>
<td>Space Charge Effects in ICP-MS</td>
<td>9</td>
</tr>
<tr>
<td>Particle Size Distribution</td>
<td>10</td>
</tr>
<tr>
<td>Matrix Effects on Accuracy</td>
<td>11</td>
</tr>
<tr>
<td>Relevance, Impact, and Technology Transfer</td>
<td>13</td>
</tr>
<tr>
<td>Project Productivity</td>
<td>13</td>
</tr>
<tr>
<td>Personnel Supported</td>
<td>13</td>
</tr>
<tr>
<td>Publications from EMSP-96 Award</td>
<td>14</td>
</tr>
<tr>
<td>Collaborations</td>
<td>15</td>
</tr>
<tr>
<td>Future Work</td>
<td>15</td>
</tr>
<tr>
<td>Particle Generation from Laser Ablation Processes</td>
<td>16</td>
</tr>
<tr>
<td>Transport of Ablated Particles to the ICP</td>
<td>17</td>
</tr>
<tr>
<td>Inductively Coupled Plasma</td>
<td>18</td>
</tr>
<tr>
<td>Qualifications of the PI</td>
<td>18</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>19</td>
</tr>
</tbody>
</table>
EXECUTIVE SUMMARY

Laser ablation can save the DOE millions of dollars in characterization costs. Chemical characterization represents a significant need within the DOE EM program in the areas of high-level waste, tanks, sub-surface contaminant plumes, D&D activities, spent nuclear fuel, mixed wastes, and plutonium disposition. Laser ablation can provide direct characterization of EM solid waste in a safe and timely manner, and at a reduced cost compared to conventional analytical procedures. The primary technical difficulties hindering laser ablation technology for EM applications are matrix dependence and fractionation, both effect accuracy of quantitative characterization. These issues were studied on a fundamental level to develop laser ablation as a routine characterization technology for EM applications. The final report summarizes the findings of the EMSP-96, which led to 15 journal publications, 1 encyclopedia chapter, 4 refereed conference proceedings, 14 invited talks, and interactions with EM personnel.

The research showed how the matrix of the sample could effect accuracy of characterization. Depending on the matrix elements, there could be an enhancement or depression of signal. A novel approach for studying matrix effects was discovered and implemented for this work. The work demonstrated how using UV lasers with short pulses could minimize fractionation. Also, the work showed how to enhance the sensitivity by using different noble gases in the ablation chamber, and by optimizing the ICP-MS for dry sample introduction. We achieved several orders of magnitude increase in sensitivity by performing these studies. The work also identified other areas that need to be studied to further develop this technology for reliable characterization of EM samples. An area of research that needs to be investigated is to define the role of ablated particles in the characterization. When a sample is ablated, particles are generated. These particles can have different chemistries and therefore will influence the analysis, depending on their size distribution.

There are numerous studies and applications involving laser ablation within the DOE laboratories and sites. The Tanks Focus Area (TFA) has contributed to the development of laser ablation inductively coupled plasma – mass spectroscopy (LA-ICP-MS) at the Pacific Northwest National Laboratory (PNNL) and Hanford Site. Los Alamos is investigating direct soil, waste-form, and plutonium
characterization using laser ablation plasma emission and ICP-MS. Savannah River also has investigated laser-ablation ICP-MS for the characterization of vitrified waste glass. The DOE Material Disposition program selected laser ablation as the technology for direct characterization of pre- and post-blend PuO$_2$ powers before ceramic formation. Argonne West has studied LA for uranium characterization. Finally, laser ablation was identified by the DOE CMST cross cutting program as a key technology for EM, and by the TFA for further developing the system at the Hanford Waste Site.

The PI (R. Russo) has established collaborations with investigators from the Pacific Northwest National Laboratory, Argonne National Laboratory and Argonne West, Savannah River Site, Los Alamos, Oak Ridge, and Sandia who can benefit from new fundamental information related to laser ablation for chemical characterization. Russo established an interaction with John Hartman, Mike Alexander, and Monte Smith, the primary personnel responsible for setting up the LA-ICP-MS system in Building 222S at PNNL. Russo visited the Hanford Site and toured the LA facility. Russo communicates regularly with personnel at the other National Laboratories working to develop the laser ablation technology. He met with Debbie Figg at LANL and contributed to discussions on the use of LA for Pu analyses. Chris Bannochie with the DOE Materials Disposition Program is developing two LA systems, at SRS and LLNL for Pu characterization. Because of the reputation of the PI and the EMSP program, Russo was asked to help develop the systems and standards for this PuO$_2$ effort. Russo also interacts with other EMSP investigators studying laser ablation, including Mike Pellin (D&D) and Scott Goode (laser-induced plasmas).
RESEARCH OBJECTIVES

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. Characterization of elemental and isotopic chemical constituents is an important function in support of tank-waste operation and remediation functions. Proper waste characterization enables safe operation of the tank farms, resolution of tank safety questions, and development of processes and equipment for retrieval, pretreatment, and immobilization of tank waste. All of these operations are dependent on the chemical analysis of tank waste (1). A specified need by the Tanks Focus Area (TFA) is to validate the laser ablation mass spectrometer (LA/MS) technology through round robin testing of standard materials and through fundamental studies of the laser ablation process (2). Advancement of the laser ablation technology is warranted to guarantee accuracy of analysis for the diversity of complex EM samples. This EMSP research endeavored 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.

Laser ablation offers direct characterization of any solid waste form in a timely manner and at a reduced cost compared to conventional analytical technologies (3-5). Numerous advantages exist for direct solid waste-form characterization. Little or no sample preparation will be required. Laser ablation will eliminate the dissolution requirement, and eliminate the generation of solvent waste. Personnel exposure to hazardous materials will be minimized. Chemical characterization
using laser ablation requires a smaller amount of sample (<micrograms) than that required for conventional solution nebulization (milligrams). Depending on the analytical detection system, picogram to nanogram quantities may be sufficient for analysis. The smaller sample requirement will also minimize contamination of equipment. Finally, because photons are used for sampling, any sample can be laser ablated. The sample can be homogeneous, heterogeneous, radioactive, stable, inorganic, organic, biological, sludge, saltcakes, soils, anything. The focused laser beam permits spatial characterization of heterogeneities in solid samples. Because of these capabilities, laser ablation has received a great deal of attention; numerous analytical studies are described and reviewed in the literature (5-18).

Within the DOE National laboratories and sites, there are many studies and applications of laser ablation. Pacific Northwest National Laboratory is studying LA-ICP-MS for characterization of sludge and other waste forms from tanks (3-4). A LA-ICP-MS system has been established at the Hanford Site for characterization of HLW (3-4) based on partial support from the TFA. Los Alamos National Laboratory is investigating direct soil, waste-form, and plutonium characterization using laser ablation plasma emission (LIBS) and ICP-MS (19-21). Savannah River also has investigated laser-ablation ICP-MS for the characterization of vitrified waste glass (22,23). The DOE Material Disposition program selected laser ablation as the technology for direct characterization of pre- and post-blend PuO$_2$ powers before ceramic formation (24). Argonne West has studied laser ablation for uranium characterization (25-27). Finally, laser ablation was identified by the DOE CMST program as a key technology for EM and by the TFA for further developing the system at the Hanford Waste Site (28).

Even with these benefits and the number of labs working to advance this technology, laser ablation is not yet suited for routine analysis of complex waste samples. The diverse HLW samples within the EM complex preclude accurate characterization without matrix-matched standards. All analytical characterization technologies require standards for calibration (9,10). For the diverse HLW samples at DOE sites, standards will not exist and it is impractical to fabricate them. Therefore, accuracy must be guaranteed by using non-matrix-matched standards. To accomplish this, one must ensure that the laser ablation process generates a chemically representative vapor from the solid sample, that the vapor is transported and detected accurately, and that the chemistry of the sample does not
influence the analysis (perturb the analytical source). The primary difficulties limiting accuracy of laser ablation with non-matrix matched standards are matrix dependence sampling and fractionation. In this EMSP-96 research, we found that laser ablation at the sample site was not the only cause of inaccurate characterization. Instead, particle size distribution, particle transport, and chemical effects in the ICP were identified as mechanisms influencing accuracy. These findings are summarized in the Methods and Results section of this proposal. Fractionation can occur at the laser ablation site, during particle condensation in the ablated vapor, during particle transport, or in the ICP-MS itself (9-11). Chemistry of the sample target will play an important role in the formation, transport and detection of particles. The particles will have different chemistries, depending on their size, whether they are formed during condensation of the atomic/molecular vapor versus directly ablated from the bulk. Work on particles in laser ablation is preliminary, yet growing because of its importance (4,9,21,29-32).

METHODS AND RESULTS

This section summarizes research performed during the three-year LBNL EMSP-96 program, as well as related literature references. Four main issues were emphasized in the EMSP-96 research to improve analytical sensitivity and accuracy, including 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. The EMSP-96 award led to 15 journal publications, 1 Encyclopedia Chapter, 4 refereed conference proceedings, and 14 invited talks.

Mass Loading

Mass loading in the ICP (change in conditions) and fractionation (preferential removal of elements or non-stoichiometric vapor production) are two critical issues that effect accuracy (9-11,33,34). When the laser beam ablates a sample, a portion of mass is transported to the ICP. If the temperature or electron number density in the ICP are perturbed by this mass, accuracy is compromised (33,34). We investigated mass loading by ablating samples using a wide range of laser properties. 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 (33,34). Using a nanosecond-pulsed Nd:YAG laser, which is similar to that used in the commercial laser ablation attachments and at the Hanford Site, we identified the laser irradiance regime in which mass loading was not significant for high-density samples (alloys). However, for NIST and SRS glasses (characteristic of waste-site materials), this same irradiance regime did cause mass loading. Mass loading effects need to be better understood to ensure accuracy of chemical analysis using laser ablation sampling.

**Fractionation**

Fractionation was investigated as a function of elemental composition in a suite of alloys and as a function of time (5, 35,36). The number of laser pulses at a fixed location on a sample and the laser irradiance significantly influenced fractionation. We found that it was almost impossible to completely eliminate fractionation from many samples, including alloys, ceramics, glasses, and other refractory materials. However, it is important to emphasize that fractionation does not preclude the use of laser ablation sampling for accurate characterization. Even though fractionation exists, it is possible to use solid standards to calibrate the ICP if fractionation from the standards is similar to that from the sample (matrix matching). We demonstrated that ICP-MS data for a suite of elements versus concentration showed a linear relationship (calibration curve) with good correlation by using NIST and three other glasses, even though fractionation occurred in all the samples (35-37).

**Sensitivity**

Analytical sensitivity was addressed by studying ways to enhance laser ablation efficiency and by optimizing the ICP-MS system for dry sample introduction (38). 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 use of different noble gases in the ablation chamber also was found to enhance sensitivity (39,40). The enhancement was found to be dependent on the laser’s pulse duration. We demonstrated enhanced sensitivity by almost three orders of magnitude by using picosecond UV compared to nanosecond IR laser ablation, with traces of helium in the argon gas. The enhanced sensitivity is beneficial for detecting trace contaminants in EM waste-site samples.
ICP-MS ion-optics optimum voltages were found to be significantly different for dry and wet ICP plasmas (38). Two orders of magnitude improvement in sensitivity were observed when the ICP-MS was tuned for solid sampling conditions. ICP conditions, such as temperature and electron number density influence the total ion current through the ion optics of the MS. Based on optically measured ICP temperature and electron number densities, total current for sampling from dry and wet plasmas was compared. For typical operating conditions, ion current for sampling from wet plasma was in the range of $0.2 - 1.0 \, \mu A$. For dry plasmas, the current was about $10 \, \mu A$. Furthermore, the average ion kinetic energies for the dry plasma were about $5 - 6 \, eV$ lower than for the wet plasma.

**Space charge effects in ICP-MS**

ICP-MS 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 (41,42). For example, determining alkali and/or alkali-earth elements in Pu or U oxides will cause space charge effects, suppressing light-elements response. In the EMSP-96 research, we qualitatively investigated space charge effects in the ICP-MS and their influence on instrumental operating conditions. The ICP-MS interface was modified using a three-grid ion energy analyzer (38). Kinetic energy of sampled ions could be measured in this way. Stopping curves for Ba and Li were measured at different Ar-gas flow rates. Ba stopping curves were found to be unaffected by changes in the Ar gas flow rate. In contrast, Li curves were effected by the flow rate. Li ions also were found to have higher kinetic energies. Space charge effects were more severe as ion current through the skimmer cone increased. Ion current decreased from about $200 \, \mu A$ to about $20 \, nA$ as flow rate was increased from 0.4 to 1.4 L min$^{-1}$. At low flow rates and high ion currents, space charge effects were strong. In contrast, the significance of space charge diminished as flow rate increased (low ion currents). As grid potential increased, the total ion current through the energy analyzer dropped. These fundamental studies were performed to understand the behavior of the ICP-MS for dry and wet conditions, characteristic of laser ablation and liquid nebulization respectively.

**Particle size distribution**

The quantity of mass removed from the sample for each laser pulse, entrainment of particles in the chamber gas flow, transport of particles through the tubing, and atomization and ionization of
particles in the ICP all influence the accuracy (and sensitivity) of laser ablation ICP-MS. The relationship between laser-generated particles and ICP-MS signal intensity was investigated by using single-pulse laser ablation sampling of Savannah River Site (Vitrification Facility) prototypical waste-glass samples (31). The particle size distribution was measured for different laser ablation conditions using an optical particle counter. For single pulse laser ablation, fewer particles were produced for the first pulse than were generated for successive pulses that repeatedly ablated the same surface location. As expected, the ICP-MS signal intensity corresponding to the first pulse was lower compared to successive pulses. The size distribution of laser-generated particles changed with laser power density and beam diameter. Laser irradiance from 0.4 – 0.5 GW/cm^2 was found to be a threshold value, over which the particle-size distribution changed. Laser beam diameter was found to be a more influential parameter than power density in efficient particle generation.

ICP-MS intensity data were calibrated with respect to the particle mass entering the torch to determine sampling efficiency (31). Particle entrainment and transport efficiency were found to be a strong function of laser irradiance (Figure 1). The efficiency decreased 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. A tradeoff exists between efficiency and fractionation.

Figure 1: Effect of the laser power density (irradiance) on transport efficiency
Matrix effects on accuracy

The chemical matrix effect on the plasma conditions was studied by optically measuring the ionic to atomic spectral line intensity ratios in the ICP \((33,34)\). The value of these ratios depends on plasma temperature and electron number densities. It was found that matrix effects for laser ablation sampling were different than for solution nebulization, because of the different nature of wet and dry ICP plasmas. Figure 2 illustrates one of the matrix effects discovered by showing the percentage ratio of Zn ionic to atomic emission in the ICP, as a function of a relative matrix amount. The effect of CaF\(_2\), MgO, and Li\(_2\)CO\(_3\) matrices were compared. In these experiments, laser ablation was performed in two chambers simultaneously. In one chamber, ablation of Zn was conducted at constant laser energy conditions (a continuous and constant amount of zinc was ablated). Laser ablation of a matrix species was conducted 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\(_2\)CO\(_3\) matrices.](image)

The Li\(_2\)CO\(_3\) matrix showed no observable change in the plasma conditions whereas CaF\(_2\) and MgO produced a drastic change in plasma conditions. In general, it was determined that Ca had a more pronounced matrix effect on the ICP than easy ionizable elements (such as Li, Na, and K). Notice that there can be a 25% error in the measurement of Zn in the presence of a high calcium matrix,
conditions that will occur in HLW samples. Once these chemical interferences are better understood, a qualitative analysis of the waste-site sample can alert the analyst to potential inaccuracies. This is one of the critical areas that will be addressed in depth in the proposed EMSP research.

The research performed for this EMSP-96 project demonstrated that a fundamental understanding of laser ablation and ICP-MS operating conditions can lead to enhanced sensitivity and accuracy of characterization. The EMSP-96 effort demonstrated that chemical matrix effects and fractionation are remaining issues that must be understood to assure 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 HLW samples.

**RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER**

Within the DOE National laboratories and sites, there are many studies and applications of laser ablation. Pacific Northwest National Laboratory is studying LA-ICP-MS for characterization of sludge and other waste forms from tanks (3-4). A LA-ICP-MS system has been established at the Hanford Site for characterization of HLW (3-4) based on partial support from the TFA. Los Alamos National Laboratory is investigating direct soil, waste-form, and plutonium characterization using laser ablation plasma emission (LIBS) and ICP-MS (19-21). Savannah River also has investigated laser-ablation ICP-MS for the characterization of vitrified waste glass (22,23). The DOE Material Disposition program selected laser ablation as the technology for direct characterization of pre- and post-blend PuO₂ powers before ceramic formation (24). Argonne West has studied laser ablation for uranium characterization (25-27). Finally, laser ablation was identified by the DOE CMST program as a key technology for EM and by the TFA for further developing the system at the Hanford Waste Site (28).

**PROJECT PRODUCTIVITY**

The research was addressed as a long-term fundamental study of underlying mechanisms of laser ablation sampling that would lead to use of this technology for EM applications. The research was
successful in identifying several important issues that influence the sensitivity and accuracy of laser ablation sampling. The underlying studies were published in scientific journals, presented at analytical meetings, and at the DOE EMSP reviews. EMSP-96, which led to 15 journal publications, 1 encyclopedia chapter, 4 refereed conference proceedings, 14 invited talks, and interactions with EM personnel.

**PERSONNEL SUPPORTED**

The EMSP award supported approximately 20% effort of the PI, approximately 20% effort of a staff plasma physicist, the full-time effort of a post-doc, the part-time effort of a graduate student, and nominal expenses for three visiting scientists. A new VG PQ3 ICP-MS was purchased and used for this project.

**PUBLICATIONS FROM EMSP-96 AWARD**


COLLABORATIONS

The PI has established collaborations with investigators from the Pacific Northwest National Laboratory, Argonne National Laboratory and Argonne West, Savannah River Site, Los Alamos, Oak Ridge, and Sandia related to laser ablation for chemical characterization. Russo established an interaction with John Hartman, Mike Alexander, and Monte Smith, the primary personnel responsible for setting up the LA-ICP-MS system in Building 222S at PNNL. Russo visited the Hanford Site and toured the LA facility. Russo communicates regularly with personnel at other National Laboratories
working to develop the laser ablation technology. He met with Debbie Figg at LANL and contributed to discussions on the use of LA for Pu analyses. Chris Bannochie with the DOE Materials Disposition Program is developing two LA systems, at SRS and LLNL for Pu. Russo was asked to help develop the systems and standards for this PuO$_2$ effort. Russo also interacts with other EMSP investigators studying laser ablation, including Mike Pellin (D&D), Scott Goode (laser-induced plasmas), and Ton Dickinson (particles). The PI will continue to interact with the numerous investigators in the National Laboratories, universities, and industries. Established collaborations will be enhanced during performance of this research to deliver this technology to EM applications.

**Future Work**

Research is warranted to focus on issues identified in our EMSP-96 research that effect accuracy of characterization; specifically, the role of chemistry and particles. Waste forms and waste-process streams will include liquids, liquids with suspended particles, sludges, saltcakes, grout, glasses, etc (1). During ablation, these different sample forms will produce a wide distribution of particles, both in terms of size and chemical composition. From the same sample, the chemical composition of large particles will differ from that of smaller particles. The particle environment will govern transport behavior and decomposition in the ICP. When particles enter the ICP, their size and composition can change the ICP conditions.

*Particle Generation from Laser Ablation Processes*

The quantity of ablated mass, the particle size distribution, and the chemistry of the particles will depend on the laser (energy, wavelength, pulse width, spot size) and sample (thermal, optical, physical) properties (5-18, 29-32, 43-47). The ablated mass will contain particles from manometers (condensed from vapor) to greater than 10 microns (spallation, phase explosion) in diameter. The particles become entrained in the carrier gas and are transported to the ICP. With different sample forms inherent to HLW, the particle environment will be diverse. Experiments are needed to measure particle ejection and particle sizes during ablation, to establish diverse particle generation conditions.
The EMSP-96 research demonstrated that the picosecond laser provided improved accuracy versus the nanosecond laser, with less significance on irradiance. An additional enhancement of the picosecond versus nanosecond laser was enhanced ablation efficiency; more mass ablated per unit energy. Based on interactions with the physics community, the PI believes that femtosecond laser pulses will provide an ideal environment for matrix independence because of the minimization of thermal effects. Preliminary research using femtosecond lasers for analytical spectroscopy has only recently been reported (48,49). Research by the physics community has demonstrated that femtosecond lasers provide a different particle size distribution that that from longer-pulsed lasers, although a comparison of the particle chemistry has not been reported.

Preliminary studies using a 266 nm Nd:YAG versus a 193 nm ArF excimer laser under closely matched ablation conditions showed better analytical characteristics at 193 nm (50,51). Reduced elemental fractionation using a 193 nm ArF excimer laser equipped with a homogenized optical array also has been reported using an ICP-TOF-MS (51). The improved analytical results may be explained by differences in the particle size distribution produced by the two lasers; an area to be investigated by this research.

Particle generation processes also depend on the sample form. For glasses, small size particles are condensed from vapor, whereas the recoil plasma interacting with the melted layer and an exfoliation process mainly produce larger particles and bulk solid flakes (31). For pressed pellets, particle generation processes also include shockwave spallation (52). For high-density alloys, thermal vaporization may dominate the formation of small particles. For ablation of single crystal silicon and NIST glass, we discovered a phase explosion process that produced large particle (~5 - 20 micron) (44-47).

CCD imaging has found application for the study of nanoparticle formation in laser plumes (53). Time-resolved particle ejection (particle velocity) and changes in particle size can be measured using this system (44-47). Particle sizes equal to and greater than the wavelength of the probe light (532nm) can be measured. For samples representative of waste-site materials (glasses, porous pressed pellets) ablated particle sizes can be as larger as 10 µm, which are easily detected by this shawdow imaging system.
Transport of ablated particles to the ICP-MS

Particles can be too large for efficient transport or large particles that are transported may not be vaporized and excited in the ICP. During the transport process, the particle size distribution can be altered by changing tube length, tube diameter, or letting the flow pass through a strong electric field (21, 54). However, only a limited amount of research has been dedicated to the effect of chemical matrix on the particle size distribution and transport (21, 32). In preliminary work, Figg showed that fractionation was effected by the particle size distribution. A small tube was inserted in the flow line, and acted as a size filter. The ratio of elements in the ICP-MS was different with and without the tube (21). The different size particles were shown to have different compositions (55). Understanding particle size distributions effects on transport to the ICP, and the chemistry of particles versus size, from laser ablation sampling is a necessary study to developing this technology.

Inductively Coupled Plasma

The EMSP-96 initiated research on the influence of matrix elements on the ICP conditions (33,34). Matrix elements with a low first ionization potential (K, Na, Rb, Cs) were found to cause signal suppression or enhancement, depending on the analyte (56-58). A new kind of matrix interference was found and seems to be correlated with the second ionization potential of some matrix elements (33,34). A mechanism has been proposed that involves interactions between the doubly charged matrix ions and argon species in the plasma (ICP). However, further research is warranted to better understand this matrix interference.

Waste samples will contain sodium, cesium, strontium, technetium, and transuranics, all of which can lead to matrix interferences in the ICP.

Qualifications of the PI

R. Russo at the Lawrence Berkeley National Laboratory has investigated fundamental laser ablation processes for 13 years and has 25 years experience related to analytical chemical analysis. He has experience studying fundamental mechanisms underlying laser ablation processes through Basic Energy Science (BES) supported research at the Lawrence Berkeley National Laboratory. The PI has
directed five PhD students, including two supported by the IMSP-96 project. The PI is regularly invited to present lectures and contribute to special issues of scientific journals, by both the physics and chemistry communities. The PI was the organizer for the Fourth International Conference on Laser Ablation, held in Monterey CA July 1997. The PI has approximately 75 publications in the area of laser ablation (135 total publications), including three book chapters, and an encyclopedia article.
LITERATURE CITED


2) http://www.pnl.gov/tfa/


24) Private communication with Dr. Christopher Bannochie, Savannah River Site, Materials Disposition Program.


28) http://WWW.CMST.ORG/


55) Robache, A; Mathe, F; Galloo, JC; Guillermo, R., Multi-Element Analysis By Inductively Coupled Plasma Optical Emission Spectroscopy Of Airborne Particulate Matter Collected With A Low-Pressure Cascade Impactor. Analyst, 125, 1855-1859 (2000).
