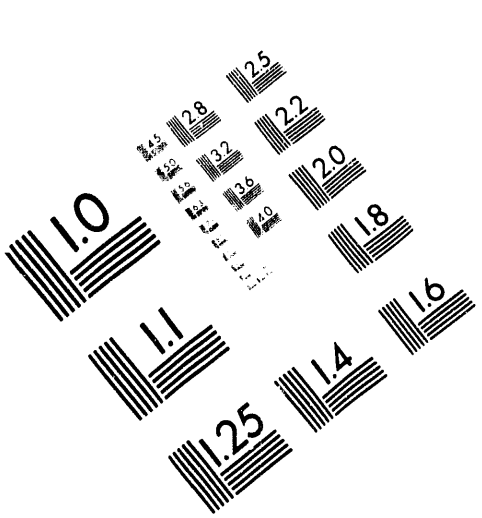

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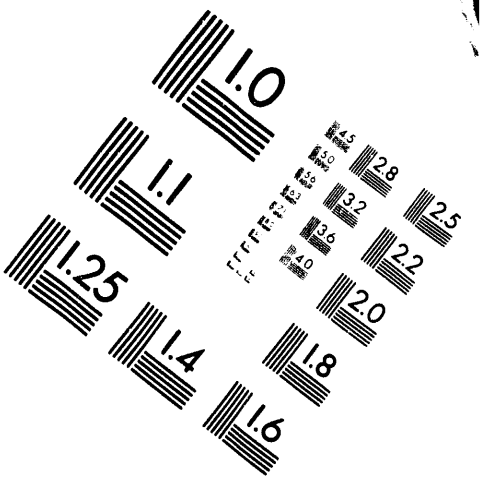

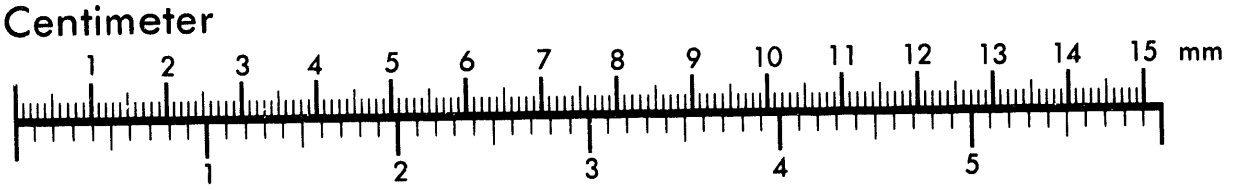

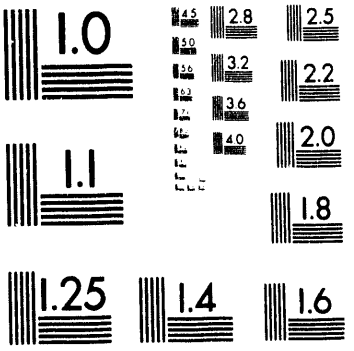

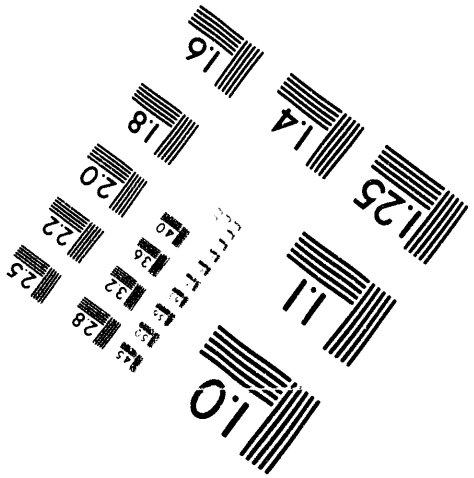

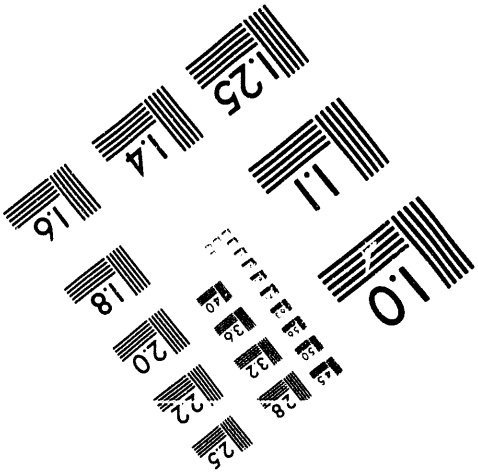

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PNL-SA-22070

UV AND IR LASER ABLATION FOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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June 1993

Presented at the
2nd International Conference
on Laser Ablation
April 19-22, 1993
Knoxville, Tennessee

Prepared for
the U.S. Department of Energy
Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

UV AND IR LASER ABLATION FOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT

Laser ablation particle plume compositions are characterized using inductively coupled plasma mass spectrometry (ICP/MS). This study evaluates the mass response characteristics peculiar to ICP/MS detection as a function of laser fluence and frequency. Evaluation of the ICP/MS mass response allows deductions to be made concerning how representative the laser ablation produced particle plume composition is relative to the targeted sample. Using a black glass standard, elemental fractionation was observed, primarily for alkalis and other volatile elements. The extent of elemental fractionation between the target sample and the sampled plume varied significantly as a function of laser fluences and IR and UV laser frequency.

INTRODUCTION

Generating particle plumes for introduction into inductively coupled argon plasma (ICP) sources for mass[1,2] or atomic emission[3,4] spectrometric analysis is one of the important analytical applications for laser ablation techniques. For practical reasons, the physical characteristics of the particle plume are important from an analytical perspective. Particulate transport, sample representation, and morphological attributes that affect the efficiency of the ICP to sequentially vaporize, atomize and ionize sampled material to be considered.

Early studies using 0.5 to 1.0 J Nd:YAG lasers operated at their 1064 nm fundamental frequency often produced ablation products with less than ideal characteristics. Ablation of geologic materials produced particles which ranged from sub-micron up to many microns in diameter. Fallout during transport and incomplete ICP vaporization posed serious problems. Gravitational and/or electrostatic losses in the transport tubing invited cross contamination and incomplete vaporization of the ablation particles and caused semiconductive coatings (glass) to form within the mass spectrometer interface and ion optics (i.e. sample/skimmer cones and lenses). Larger particles were surmised to have been produced by excessive IR light penetration with consequential surface cracking and subsurface expansion. In addition to the generation of large and widely varying particulate size ranges, we have also observed significant elemental fractionation, indicating preferential ablation or vaporization of volatile species. Increased sensitivities of these volatile elements suggest that these elements evolved by thermal evaporation processes or simply that these elements, once ablated, exist as or condense on smaller particulates that are more efficiently transported to the ICP and are subsequently vaporized with higher efficiency by virtue of their relatively higher surface concentrations.

Due to these deleterious IR laser plume characteristics, higher frequency lasers have been investigated in our laboratory for ICP/MS analysis

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*Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

of silicate materials. Favorable results with regard to producing finer, more ICP-vaporizable particulates with negligible volatile species fractionation have been obtained. Although the UV laser has provided better solid sampling attributes for ICP/MS analyses, experiments which evaluate both IR and UV laser induced plumes as a function of fluence were required to better evaluate ablation processes. This paper describes our initial attempt to compare ablation plume compositions produced by varying laser fluences and frequencies.

EXPERIMENTAL

A schematic diagram illustrating the generic laser ablation ICP/MS configuration is shown in Figure 1. The laser is focused on the surface of a sample located within the sample cell. The cell, constructed with an optic grade quartz window, provides a gas seal to be formed to assure argon carrier gas flow through the cell such that the ablated sample material can be transported to the ICP/MS. The x-y-z translational stage can be operated manually or computer controlled to allow sample focusing (z stage), rastering (bulk area), and selected spacial analysis capabilities.

The instrumentation used for these evaluations include a Fisons Inductively Coupled Plasma Mass Spectrometer (ICP/MS, VG PlamaQuad PQ2+), a Spectron Laser Systems SL400 500 mJ Nd:YAG laser and a Potomac Photonics model UV-1000 60 μJ KrF excimer laser. The Nd:YAG laser characteristics include fundamental frequency (1064 nm) operation with a multimode beam and fixed Q pulses (150 μs). The KrF excimer laser system provided a fundamental frequency of 248 nm with characteristic pulse lengths of about 50 ns.

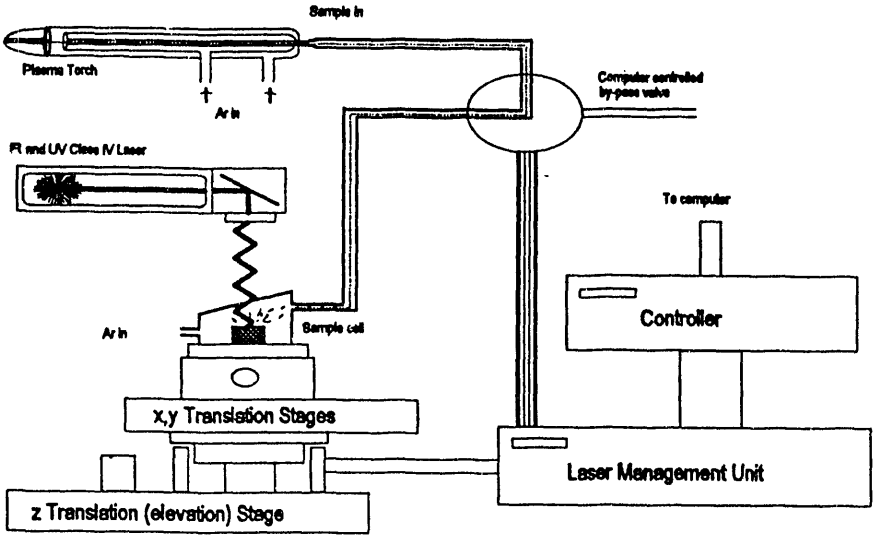

Fig. 1 Laser ablation ICP system configuration. Optical emission or ion sampling of ICP can be performed for analysis purposes.

Conventional ICP/MS operating conditions (e.g., RF power, gas flows, scanning parameters, etc.) were utilized with the exception that carrier gas flow (i.e., nebulizer gas) of 1.2 L/min.was used rather than the more conventional 0.7 to 0.9 L/min. flow rates. Laser fluences were determined directly via a Scientech power meter employing UV and IR calorimeters. Incident beam diameters were estimated by measuring respective ablation pit diameters. The material used for this investigation was a Hanford simulated waste glass, synthesized to represent expected nominal waste glass compositions without actual radioactive constituents. The expected (target values) concentrations and UV laser ablation ICP/MS determinations for this glass are shown in Table 1. Optical absorption studies indicate that this glass is significantly more opaque to UV relative to IR light.

RESULTS

To evaluate laser ablation plume compositions as a function of laser frequency and/or fluence, the ICP/MS detection characteristics must be determined in order to allow distinction between instrumental detection sensitivity and laser ablation sampling effects. The instrumental mass response patterns shown in Figure 2 illustrate detection sensitivities as a function of mass and laser parameters. Each of these curves were determined by fitting quadratic equations to x-y plots of isotopically normalized count rates of refractory glass components (e.g., Si, Mg, Fe, Zr, Al, Sr, Y, Ba, and rare earth elements) and their respective masses. Only elements that were presumed to exist as refractory oxides were used to construct the mass response curves such that these curves portrayed instrument response characteristics rather than potential laser ablation sampling effects. As seen from Figure 2, the IR and UV laser ablation responses are similar, but not identical, and approximately 3 to 10 times more IR fluence was required to yield similar UV ablation sensitivities.

Evidence for elemental fractionation resulting from laser sampling can be inferred by plotting the ratio of each element's measured count rate to that expected from the calculated refractory element curves at their respective masses. Using this approach, apparent fractionations are observed for several elements in Figures 3 and 4. Ruthenium fractionation is evident for both IR and UV induced laser plasmas, particularly at near-ablation threshold fluences.

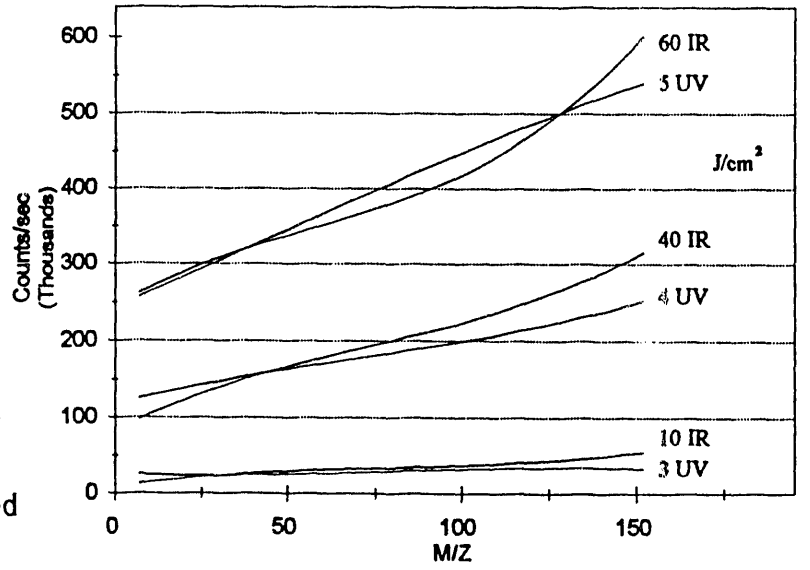

Fig. 2 IR & UV laser ablation ICP/MS mass response curve dependence on laser fluence

Similarly, the UV ablation results suggest other elemental fractionations are more pronounced when low-laser fluences are used. Contrary to UV element trends and the Ru-IR trend that suggest less sample fractionation occurs as laser fluences are increased, other IR element trends indicate less representative sampling with increasing IR laser fluence. The results reported in Table 1 were performed at the maximum UV laser fluence (i.e., 5 J/cm^2). Good agreement between the measured concentrations, in particular Ru, Cs, Rb, Rh, and Cd, and targeted concentrations validates the case for using higher UV laser fluences for accurate laser ablation sampling of this material.

Table I Analysis of Simulated Waste Glass (CVS I-19) using UV Laser Ablation ICP/MS and Energy Dispersive X-ray Fluorescence (EDXRF)

Element	Target (Wt %)	Measured LA-ICP/MS (Wt %)	Error	RSD (%) (N=3)	Measured EDXRF (Wt %)
Si	22.44	21.8	3.7	17	25.6
B	3.55	3.6	0.1	3	
Li	1.75	1.93	0.04	2	
Ca	1.97	1.95	0.05	3	2.2
Mg	2.19	2.3	0.01	4	
Fe	3.97	4.01	0.09	2	4
Zr	3.18	3.16	0.11	3	3.39
Al	3.37	4.05	0.07	2	<4.5
Cr	0.062	0.063	0.001	2	
Mn	0.069	0.069	0.003	4	
Ni	0.33	0.42	0.05	12	0.32
Cu	0.10	0.20	0.02	10	0.08
Rb	0.034	0.034	0.002	6	0.028
Sr	0.062	0.062	0.01	16	0.052
Y	0.029	0.029	0.001	3	0.029
Mo	0.146	0.15	0.007	5	0.85
Ru	0.083	0.083	0.006	7	0.078
Rh	0.028	0.027	0.002	7	0.019
Pd	0.032	0.31	0.003	10	0.054
Cd	0.479	0.48	0.02	4	0.613
Cs	0.103	0.12	0.004	3	0.105
Ba	0.065	0.068	0.003	4	0.059
La	0.388	0.39	0.02	5	0.352
Ce	0.089	0.083	0.011	13	0.079
Pr	0.060	0.063	0.004	6	
Nd	0.771	0.79	0.02	3	
Sm	0.032	0.032	0.002	6	

DISCUSSION

The obtained results indicate that laser induced fractionation mechanisms are occurring during ablation of multi-component glass matrices, such as the one studied here. Low ablation fluences with UV or IR lasers do not produce particle plumes that are completely representative of complex target material, as evidenced by the initial evolution of Ru, and other constituents observed in Figures 3 and 4. However, increasing the laser fluence may not produce optimal results either, as exemplified by the IR experiments, which suggest preferential ablation of Rb, Cs, and Cd as fluences are increased. Because this trend was not observed for the UV sampling, this effect is presumably related to the sample's optical absorption properties.

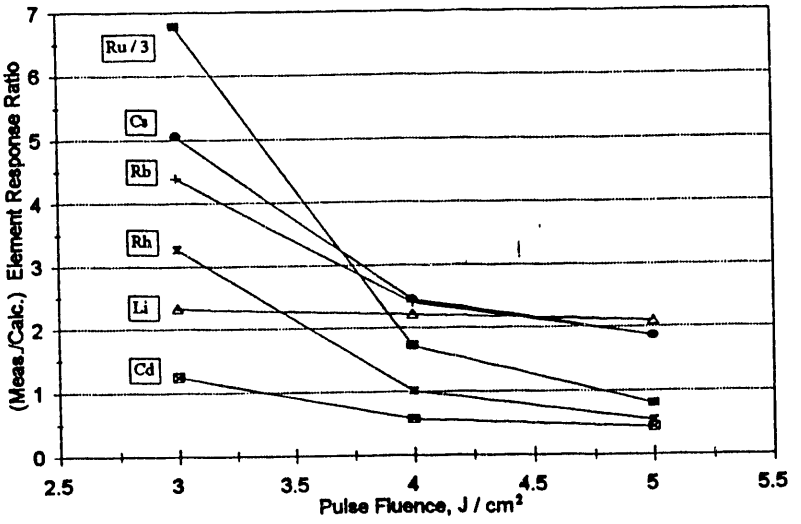

Fig. 3 UV laser ablation element fractionation as a function of laser fluence.

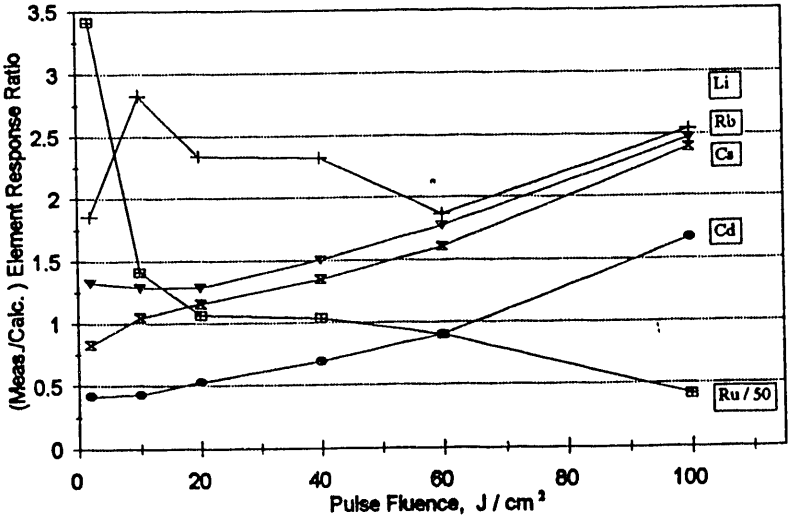

Fig. 4 IR laser ablation element fractionation as a function of laser fluence.

Another observation provided by these preliminary investigations is the lack of Li fraction for both IR and UV experiments. Although the Li results obtained for the IR experiments are difficult to evaluate due to their sporadic trend (Figure 4), the UV results argue that preferential ablation of this element does not occur. A probable explanation for this element's behavior is that Li glass components are less volatile than the associated Rb and Cs components.

The laser-sample interactions portrayed through the observed trends are indicative of thermal effects. From this study, laser light which is highly absorbed by the sample is less prone to selectively ablate volatile constituents, provided that fluences significantly exceed the ablation threshold values are used.

CONCLUSIONS

Laser induced element fractionations, as determined by ICP/MS, were most noticeable at low fluences. By investigating ablation plume compositions produced by substantially different laser frequencies (i.e., IR and UV) we observed that the degree of elemental fractionation is dependent on the target sample's potential to absorb the incident laser light. Consequently, for analytical applications, lasers employing frequencies which are highly absorbed by the target material are more likely to provide particle plume compositions which are more representative of the target sample. Finally, our results indicate that good analytical results can be obtained using UV laser ablation to sample simulated Hanford waste glass.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Hanford Waste Vitrification and the Tank Waste Remediation programs for the support of this work.

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