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Formerly CETAC

14306 Industrial Road
Omaha, NE 68144
USA
PHONE 402.733.2829
FAX 402.733.5292
WWW CETAC.com

Application Note

Signal Uniformity in an Active Two Volume Laser Ablation Cell

Dhinesh Asogan[1], Steve Moody[1], David Clarke[1], John Roy[2], Steve Shuttleworth[2], Damon Green[1]

[1] Teledyne CETAC Technologies, 14306 Industrial Road, Omaha, NE 68144, USA, dasogan@cetac.com

[2] Teledyne Photon Machines, 366 Gallatin Park Drive, Bozeman, MT 59715, USA

INTRODUCTION

Laser ablation as a solid sample introduction technique has always been limited by the sample chamber employed to transport the generated aerosol to a connected ICP-MS. The plasma torch, historically, is intolerant of air in the central channel. Whilst instrumentation is improving apace, isolating the sample from air is still important. Additionally, effective ablation occurs under helium atmosphere. Both these factors mean that an isolated chamber is required.

Enclosed chambers have a limitation with regard to aerosol transport. To fit larger samples or a larger number of samples, the chamber has to be made larger in size. Laser plumes expand at supersonic speeds initially, meaning the aerosol will expand to fill the ablation volume quickly. This reduces effective signal intensity and increases washout time, which also increases the likelihood of cross contamination between samples.

One way to combat this is to use a 2-volume cell. A large outer box is used to house the samples and a small inner volume (the 'cup') where the ablation occurs. The cup constrains the aerosol so that signal intensity and washout are not adversely affected. The cup is fixed centrally under the laser beam by means of an arm that enters the outer cell and serves as the cell output.

The HelEx Active 2-Volume Cell employs two independently controlled gas flows: one to the outer chamber to keep it purged and under positive pressure, and another to the cup to control the aerosol. The HelEx II is an iteration of the original HelEx design. It has a range of cup inserts that allows the user to tune the ablation volume to the application being run.

In this study, the positional variation of data quality was assessed using HelEx II cup design installed onto a Teledyne CETAC Technologies LSX-213 G2+ Solid State Laser Ablation System. Washout and signal reproducibility was assessed over nine regions of the sampling area, using statistical tests to assess the significance of any variability seen.

EXPERIMENTAL

Nine NIST 612 glasses were polished and loaded into the HelEx Active 2-Volume Cell in a grid covering nine regions of the cell sampling area. The system was tuned to minimize fractionation using the central NIST glass by monitoring the ratio of Th/U and ensuring it was close to 1.08. This central NIST glass was used as the reference point for subsequent comparisons. Tune settings are summarized in Table 1.

The regions were assigned as shown in Figure 1. For assessing regional reproducibility and washout, 4 line scans were obtained at each region of the sampling area. Each line scan was assessed for washout by fitting

an Extreme Value Pulse function to the washout region of the signal trace:

$$I = I_p e^{-e^{-\frac{t-t_p}{c}} - \frac{t-t_p}{c} + 1}$$

Where:

I is the Signal Intensity,

I_p is the Peak Signal Intensity,

t_p is the time at which the Peak Intensity occurs

and c is a Peak Width factor

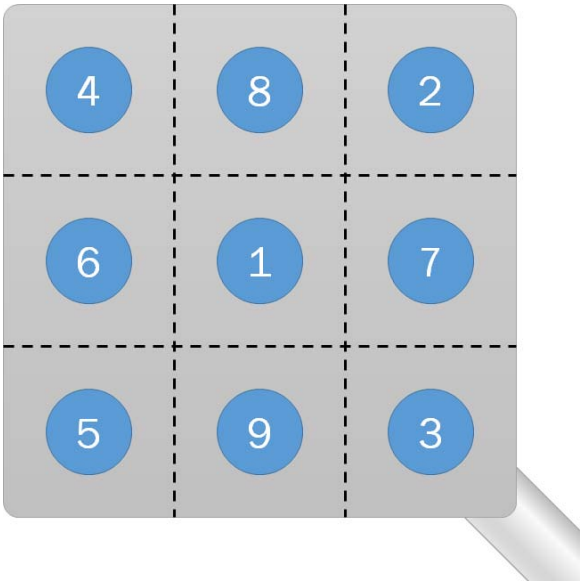

Figure 1. Cell sampling region assignments

The investigation was performed under purged and insufficiently purged condition. Complete purging was achieved using three 7 second cycles of the in-built vacuum pump. One cycle evacuates the cell to approximately 7 psi absolute pressure, then is back filled with all three mass flow controllers running at 1 L/min to flush the cell. This pushes air and water vapor out of the cell.

For "insufficient purge", one cycle was run to the point where switching the system onto 'online' mode did not extinguish the plasma, thereby providing the maximum air/water vapor/helium mix that could be handled by the plasma. This was timed to be 3 seconds.

Table 1. Instrument Settings

Thermo iCAP-Q ICP-MS	
Forward Power	1350 W
Cool Gas Flow	14 L/min
Aux Gas Flow	0.8 L/min
Sampling Depth	5 mm
Nebulizer Gas Flow	0.12 L/min
Dwell Time	10 ms
CETAC LSX-213 G2+ LA System	
Laser Power	20% (8.12 J/cm²)
Spot Size	100 µm
Scan Rate	Reproducibility Study: 10 µm/sec
Outer Cell Flow	300 ml/min helium
Inner Cup Flow	500 ml/min helium
Additional Cup Flow	400 ml/min argon
Repetition Rate	20 Hz

RESULTS AND DISCUSSIONS

Representative Signal TRA traces for all nine regions are presented in Figure 2 and Figure 3. Regions 1 through 9 are represented as a single TRA trace for each region from left to right. The traces show little variability between, and statistical tests on these regions showed ***no statistical significance*** in the minor variation seen. Washout was consistent, varying from 0.96s to 1.11s between the nine regions and having ***statistically identical*** washout. In addition, the Th/U ratio varied from 1.025 to 1.076, which approximately ±2% around the mean of 1.059. Statistical tests on these values also showed no statistical difference between the regions or Th/U ratio.

Interestingly enough, "insufficiently purging" the cell did not have any effect on data quality during this study. The signal intensities are all on the same order of magnitude for the respective elements, and there is no discernible background or signal drift. Statistical tests also showed that the signal intensities, washout and Th/U ratios were statistically identical.

Figure 2. Signal Uniformity over nine areas of a fully purged HelEx II cell.

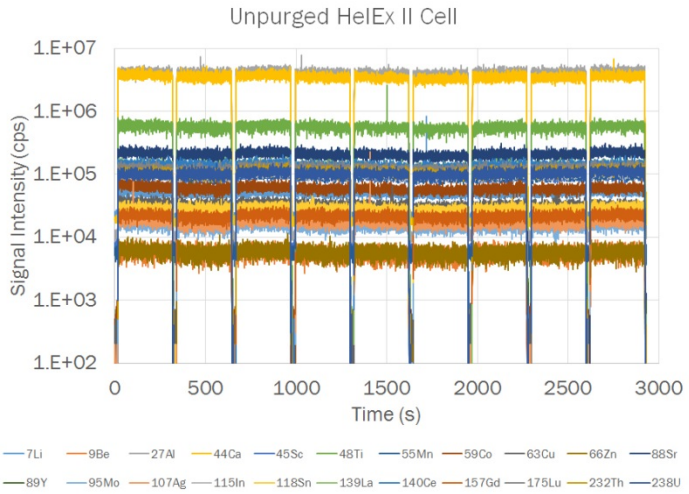

Figure 3. Signal Uniformity over nine areas of an insufficiently purged HelEx II cell.

CONCLUSIONS

Using the HelEx II Cup Inserts, data quality over the HelEx II Active 2-Volume Sampling Chamber is consistent over the entire sampling area. A 'plunger' effect cannot be identified in the data as the arm moves in and out of a purged cell. Insufficiently purging the outer chamber should have some effect of data quality as the composition stabilizes over time; however, the HelEx II cup insert appears to mitigate or buffer stabilization and maintain data quality over the cell sampling area.