Environmental Management Science Program

Project ID Number 55205

A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals

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Research Objective

The long-term goal of this project is to develop a system to measure the elemental composition of unprepared samples using laser-induced breakdown spectroscopy, LIBS, with a fiber-optic probe.

Research Progress and Implications

Research Accomplishments (Year 2)

- Fabrication of Second LIBS Spectrometer (High Spectral Resolution Echelle Instrument)
- Preliminary Design for LIBS in Aqueous Solutions
- Use of Acoustic-Optical Tuned Filter for Spatial Resolution
- Measuring the Influence of the Matrix on LIBS Signals

Research Accomplishments (Year 1)

- First Demonstration of LIBS Imaging Using Fiber Optics
- Combined LIBS and Raman Spectral Imaging in a Single Probe
- Established a Collaboration with David Cremers at LANL
- Developed a Method to Improve Launch Efficiency of High-Power Laser Pulses into an Optical Fiber Without Catastrophic Damage
- Applied AOTF to Plasma Imaging to Characterize the Plasma both Spatially and Temporally
- Development work near completion for high-resolution LIBS spectrometer.

Planned Activities

- Development of methods that can be used to mesure LIBS signals from aqueous solutions will continue.6/98-6/99
- Studies in progress to measure mass ratios of vaporized materials via dissolution followed by ICP-MS 6/98-12/98
- Evaluate the role of materials factors, such as case=hardeining-on the laser volatilization process 6/98-6/99
- Continue the study of crater size and correlate with both LIBS signal and with mass of material vaporized. 6/98-6/99
- Measure the spatial and temporal dependence of signals and background as a function of the experimental parameters. 6/98-6/99
- Evaluate spatial discrimination, in place of time resolution, as a tool that can be used in concert with high resolution spectroscopy to acquire LIBS signals. 12/98-6/99
- Continue the development of analytical methods for applied chemical analysis. 6/98-6/99

A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals

Scott R. Goode and S. Michael Angel

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Publications Resulting From or Related to this Work

Brian J. Marquardt, Dimitra N. Stratis, David A. Cremers, and S. Michael Angel, "A Novel Probe for Laser-Induced Breakdown Spectroscopy and Raman Measurements Using an Imaging Optical Fiber," Appl. Spectrosc. in press (1998).

B.J. Marquardt, B.M. Cullum and S.M. Angel "Fiber-Optic Probe for Determining Heavy Metals in Solids Based on Laser-Induced Plasmas," in Proceedings, European

Symposium on Environmental Sensing III, Munich, FRG, June 16-20, 1997, SPIE 3105-40 (1997).

Brian J. Marquardt, Scott R. Goode and S. Michael Angel, "In-Situ Determination of Lead in Paint by Laser-Induced Breakdown Spectroscopy Using a Fiber-Optic Probe," Anal. Chem., 68, 977-981 (1996).

Ph.D. Dissertation: Brian Marquardt, "Remote In-Situ Laser-Induced Breakdown Spectroscopy Using Optical Fibers." 11/7/97

Conference Papers Resulting from this Work

Brian J. Marquardt, Brian M. Cullum, David A. Cremers and S. Michael Angel, "Fiber-Optic LIBS/Raman Imaging Probe for In-Situ Elemental Microanalysis," The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, March 1-5, Abstract 942 (1998).

Dimitra N. Stratis, Brian J. Marquardt, and S. Michael Angel, "Temporal and Spatial Characterization of Laser-Induced Plasmas," The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, March 1-5, Abstract 268 (1998).

B.J. Marquardt, B.M. Cullum and S.M. Angel "Fiber-Optic Probe for Determining Heavy Metals in Solids Based on Laser-Induced Plasmas," in Proceedings, European Symposium on Environmental Sensing III, Munich, FRG, June 16-20, 1997, SPIE 3105, Paper #40 (1997).

S. Michael Angel, H. Trey Skinner and Brian J. Marquardt, "Imaging Spectroscopy Using Optical Fibers," invited talk in the Anachem Award Symposium, 24th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 26-30, Providence, RI, Abstract 305 (1997).

Brian Marquardt, Brian M. Cullum, Tim J. Shaw and S. Michael Angel, "Spatial and Temporal Profiling of Laser-Induced Plasmas," 24th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) October 26-30, Providence, RI, Abstract 353 (1997).

S.M. Angel, H.T. Skinner and B.J. Marquardt, "Imaging Spectroscopy Using Fiber-optic Probes," Microscopy and Microanalysis, Cleveland, Invited Paper 623, OH, August, 1997.

Brian J. Marquardt, Scott R. Goode and S. Michael Angel, "Spatial Profiling of Laser-Induced Plasmas for the Purpose of Optimizing Fiber-Optic LIBS Probe Designs," The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, Georgia, March 16-21, Abstract 816 (1997).

Brian J. Marquardt, Scott R. Goode, Timothy J. Shaw and S. M. Angel, "The Development of an In-Situ Method for Elemental Analysis Using Laser-Induced Breakdown Spectroscopy," 23rd Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Sept. 29-Oct. 4, Cincinnati, Ohio, Abstract 581 (1996).

Brian J. Marquardt, Scott R. Goode, Timothy J. Shaw and S. M. Angel, "The Development of a Method for Remote Elemental Analysis Using Laser-Induced Breakdown Spectroscopy," 23rd Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Sept. 29-Oct. 4, Cincinnati, Ohio, POSTER Abstract 390 (1996).

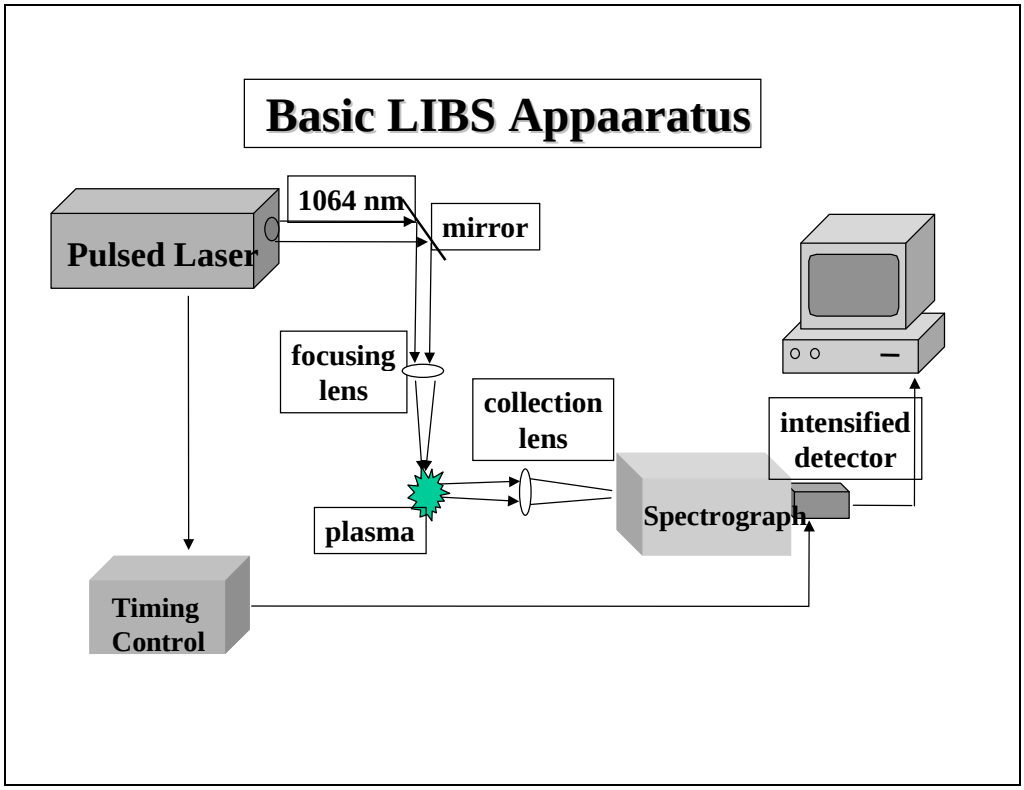
Patent Disclosure

Brian J. Marquardt, Scott R. Goode, and S. Michael Angel, "On-Site Determination of Lead in Paint Using a Novel Optical Fiber Probe," disclosed September 1996.

Characterizing Laser-Induced Plasmas Using Temporal, Wavelength, and Spatial Resolution

For LIBS to realize its full potential for elemental analysis, the events leading to the generation of the optical signal must be studied and understood. One of the most important questions facing the users of this (of any) analytical tool is whether the sample matrix influences the analytical results. If the analysis is matrix independent, then 2.0% lead in paint produces the same signal as 2.0% lead in steel. Although the matrix effect could possibly be studied empirically, fundamental studies of the laser induced breakdown spectroscopy provide a much more organized basis to answer this, and many other questions. A typical LIBS apparatus is shown in Figure 1.

Figure 1. LIBS System. The LIBS experiment uses a pulsed laser closely focussed on a sample to form a plasma. The emission from the plasma is viewed by a spectrograph and detector system.



Development and Use of an Acousto-Optic Tunable Filter to Study LIBS Phenomena

Factors affecting the LIBS signal are being investigated using a time-resolved imaging spectrometer that uses an acousto-optic tunable filter (AOTF) along with a gated intensified charge-coupled device (ICCD). This apparatus, shown in Figure 2, has been used successfully to determine how the emission of lead in a sample changes from the first to the second, to the third, to the 100th laser pulse at the same spot.

Figure 2. Acousto Optic Tunable Filter LIBS Spectrometer. This apparatus provides a spatial map of emission at a particular wavelength and time after the laser pulse.

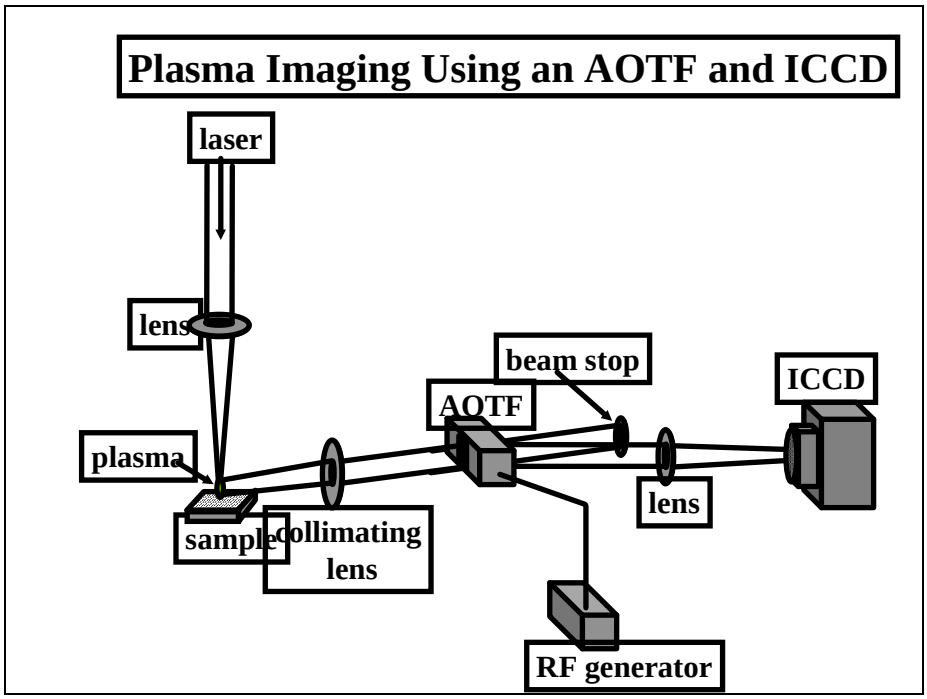
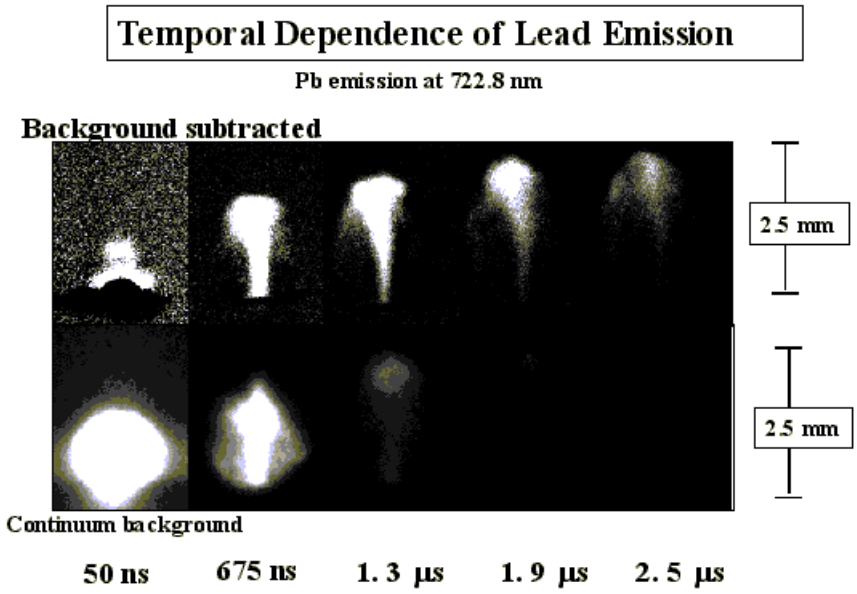


Figure 3 shows images of the plasma emission obtained under the same conditions with the exception of the number of times the same region was sampled. For these experiments, the laser repetition rate and laser powers were held constant at 2 Hz and 300 mJ per pulse (7ns) respectively. In addition, the plasmas were formed using the

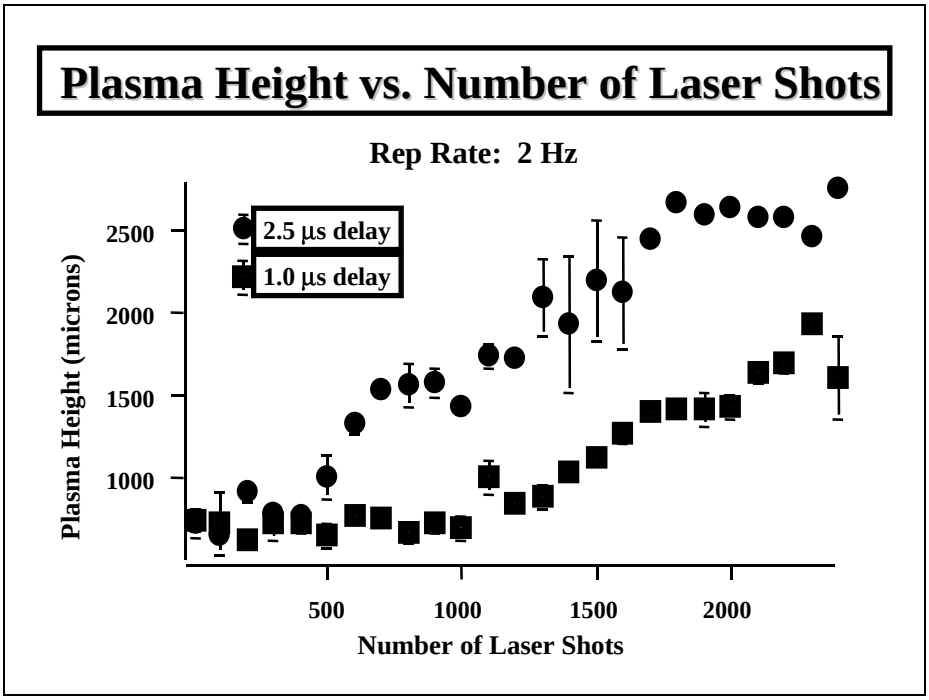
fundamental 1064 nm output of a Nd:YAG laser and the images were acquired 2.5 µs after the laser pulse over a 250 ns gate width. As can be seen, the height of the lead emission observed from the 100th sampling to the 2400th sampling of the same region increases significantly from 0.63 mm to 2.75 mm.

Figure 3. Lead Emission. The background-subtracted lead emission rises and diffuses as a function of time.



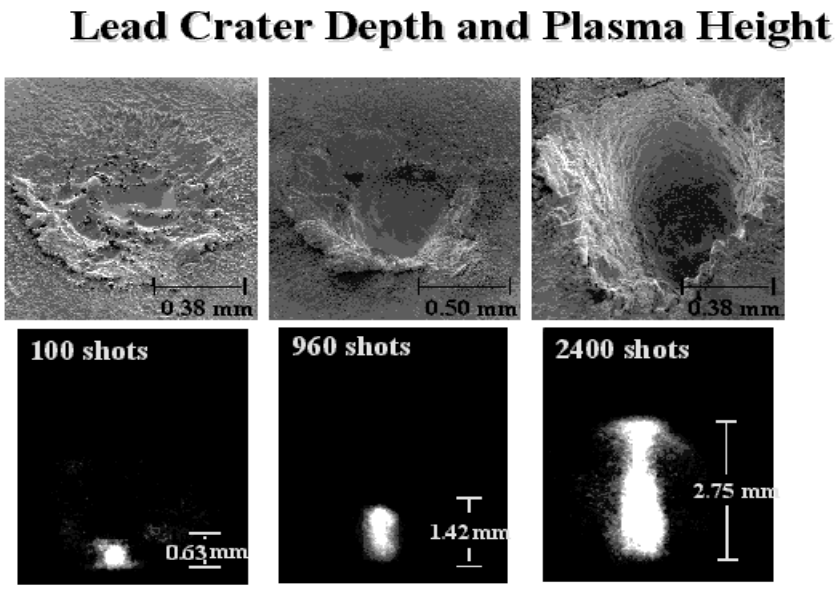
This effect is summarized in Figure 4 for two different delay times. The same general trend of increasing plasma emission height is observed at the 1.0 µs as well as the 2.5 µs delay times. In addition, the 2.5 µs delay time plasma images are overall higher than the 1.0 µs delay time since the plasma has expanded and grown up over time.

Figure 4. Growth in plasma height with repeated laser pulses. The plasma emission plume becomes larger with repetitive laser pulses



The change of the plasma emission intensities seems to be related to the size and shape of the crater that is formed in the lead sample. Figure 5 shows SEM (scanning electron microscopy) images of the lead craters corresponding to the plasmas shown in the bottom of the figure. A rough estimation of the crater depths which correspond to these images vary from approximately 0.1 mm for 100 laser shots to about 1 mm for 2400 laser shots. One explanation for the signal enhancement is that increasing laser shots causes deeper craters with a defined shape that may act to funnel the ablated material preferentially in the direction of the incoming laser beam. This would increase the laser/particle interactions and thereby increase the excitation and emission observed.

Figure 5. Crater depth and plasma height. Both the depth of the crater and the height of the plasma increase. Each of the exposures corresponds to the same energy, but the prior history has changed.



High Resolution Studies of the Effect of the Matrix on Sampling

A high-resolution instrument that utilizes an echelle spectrometer for wavelength dispersion was fabricated. The detector is a Charge Induced Device with 256k pixels (512 x 512). The two-dimensional spectrum of a LIBS signal obtained from a steel sample is shown in Figure 6.

Figure 6. LIBS Spectrum. 100 pulses to a steel sample produces this two-dimensional echellogram

Interactions Between Sample Composition, Pulse Power, and LIBS Emission

It is rational to ask if the composition of the sample influences the mass of material vaporized. Intuitively, it seems logical that the mass of material vaporized by each laser pulse depends on factors such as volatility, but these differences are obviated by ratio techniques. A series of brass standards (certified reference materials) were analyzed by LIBS to determine how the composition influences the atomization process. The standards are primarily binary alloys, with the concentration of zinc ranging from a low of 2.86% to a high of 39.7%. The remainder of the sample is copper. Since zinc is far more volatile than is copper, the high-zinc standards may behave differently than the low zinc

standards. The zinc-to-copper emission ratio, however, should be proportional to the zinc-to-copper concentration ratio. If not, then the ruggedness must be evaluated and robust conditions located.

One of the most important factors to vary is the power of the laser pulse. The effect of the laser pulse power is controlled by the Q-switch delay; the data shown range from 20 to 100 mJ per pulse. Figure 7 show the zinc-to-copper emission ratio as a function of pulse power for brass samples containing low, medium, and high levels of zinc. These data show that samples with high amounts of zinc show a greater dependence on power than do samples with lower amounts of zinc. This study also shows that if the power exceeds a particular threshold, then the zinc-to-copper ratio is unaffected by small variations, and these conditions are robust.

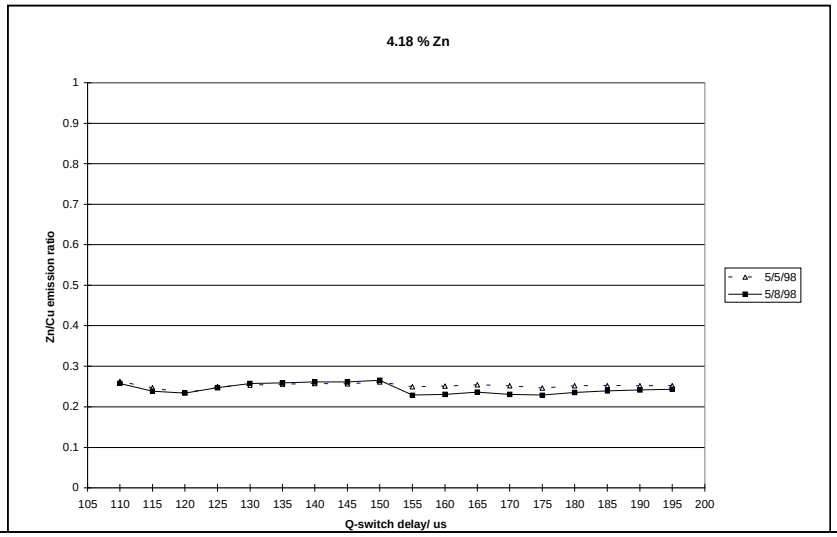


Figure 7A. 2.86% Zinc

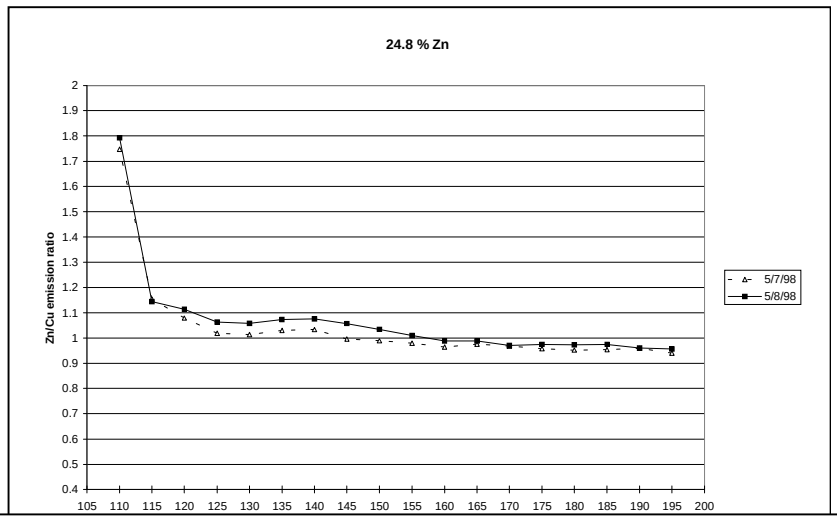


Figure 7B. 24.2% Zinc

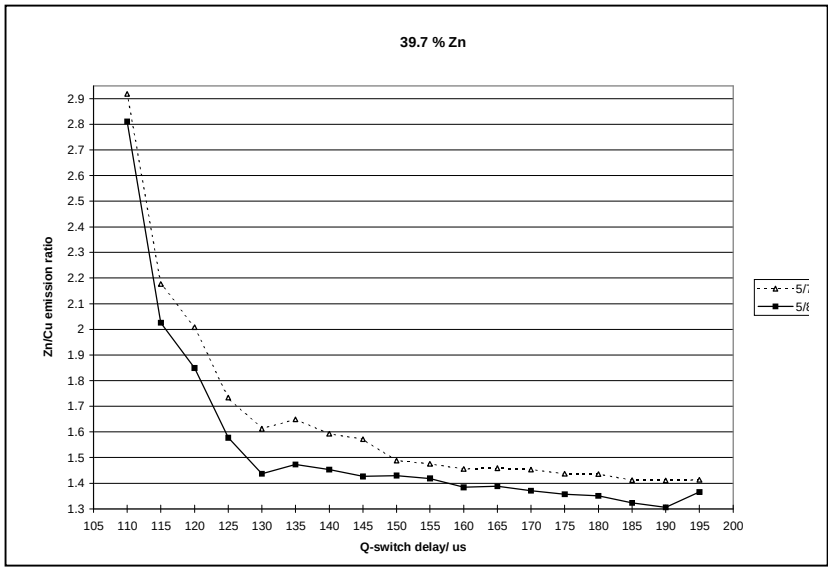


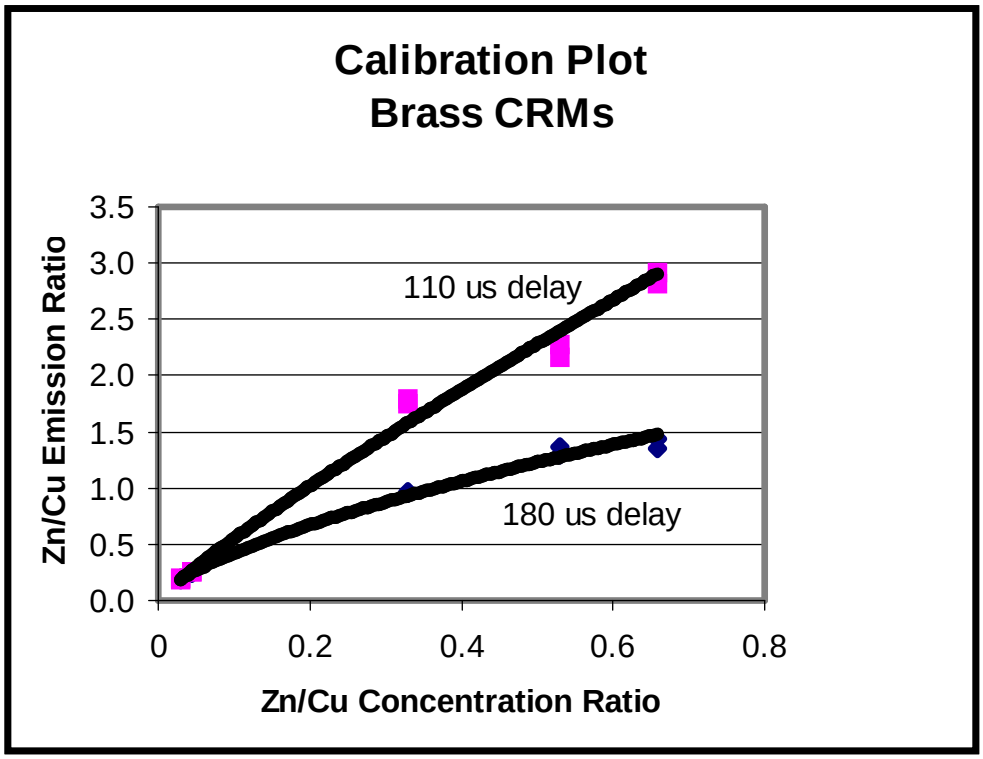
Figure 7C 29.7% Zinc

Duplicate measurements (consecutive days) to determine the effect of laser pulse power on the zinc-to-copper emission ratio for brass samples with different zinc concentrations.

When the power exceeds a threshold, small variations in power do not influence the emission ratio.

The data can be used to obtain a calibration graph, shown in Figure 8. The calibration is generally linear and can be used for chemical analysis.

Figure 8. Calibration Plot for Brass Certified Reference Materials. All data obtained with different Q-switch delays.

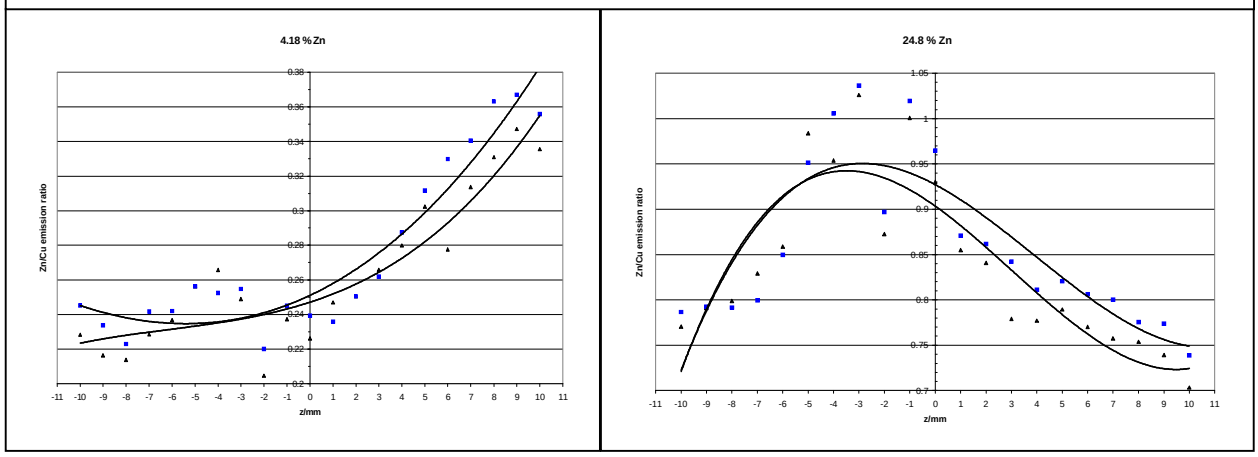


Interactions Between Sample Composition, Focal Position, and LIBS Emission

A second study, that uses a different method to control the laser pulse power, raises some surprising results. Figure 9 shows the effect of changing the focal position. The data were obtained by moving the focal lens (see Figure 1) which has the effect of changing the power density at the sample. The zero position indicates the laser is focused at the surface, a negative value indicates that the focal point is below the surface and a positive value indicates that the focal point is above the surface.

Figure 9. Effect of Focal Position on LIBS Signal. At low zinc concentrations, the focal point is a minimum in zinc-to-copper ratio. At high zinc concentrations, the focal point is near a maximum.

A. 4.86% Zinc **B. 24.2% Zinc**



Additional studies, including chemical analysis of the vaporized material, are now in progress.