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

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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 Objectives

- Develop a fiber-optic imaging probe for microanalysis of solid samples.
- Design a time-resolved plasma imaging system to measure the development of the LIBS signal.
- Setup a laboratory system capable of timing two lasers independently, for optimizing and characterizing dual-pulse LIBS.
- Compare the development of laser-induced plasmas generated with a single laser pulse to the development of laser-induced plasmas generated with a pre-ablation spark prior to sample ablation.
- Examine the effect of sample matrix on the LIBS signals of elements in different sample matrices.
- Investigate the effect of excitation wavelength of the ablation beam in pre-ablation spark dual-pulse LIBS experiments.
- Determine the effect of the physical properties of the sample on the mass of materials ablated.

Research Progress and Implications

- **Developed fiber-optic LIBS and Raman imaging probe for remote analyses.**

We developed a unique fiber-optic probe that is capable of acquiring both LIBS and Raman spectra with spatial resolution. This probe was used to demonstrate the first simultaneous measurement of LIBS and Raman spectra and images. The design and implementation of the fiber-optic probe for obtaining LIBS spectra, Raman spectra, and Raman images has been described in *Appl. Spectrosc*. and a paper in *J. Raman Spectroscopy* includes results from the Raman portion of the LIBS/Raman microprobe.

- **Acquired time-resolved single pulse laser-induced plasma imaging experiments.**

We have successfully used time-resolved plasma imaging to measure the development of the LIBS signal.

- **Investigated collinear dual-pulse LIBS.**

We have fabricated a laboratory system to time two lasers independently for optimizing and characterizing dual-pulse LIBS. We have successfully produced enhanced emission signals over conventional, single pulse experiments for a number of different samples.

The dual pulse collinear LIBS work has been published in *SPIE Proc.*

- **Developed new pre-ablation dual-pulse LIBS technique for enhanced ablation and emission**

A new dual-pulse LIBS technique that gives enhanced LIBS signals for a large variety of samples has been investigated. This exciting research has resulted in a number of papers and conference presentations. A patent disclosure on the pre-ablation spark, dual-pulse LIBS technique has also been submitted.

- **Performed time-resolved pre-ablation spark plasma imaging experiments.**

We have begun to compare laser-induced plasmas generated with a single laser pulse to the development of laser-induced plasmas generated with a pre-ablation pulse. These experiments show very large increases in the overall plasma emitting volume for pre-ablation spark dual-pulse plasmas compared to conventional single pulse in experiments for both copper and lead samples.

- **Examined the effect of sample matrix on the LIBS signals.**

We studied the enhancements of the relatively volatile zinc compared to the less volatile copper in samples of brass while varying the irradiance and it appears that the sample matrix can have a large effect on the extent of signal enhancement.

- **Examined the effect of excitation wavelength of the ablation beam in pre-ablation spark dual-pulse LIBS experiments.**

We have determined the effect of changing the laser wavelength used for ablation in the dual-pulse experiments. For all samples we have tested so far there is little or no enhancement when the ultraviolet ablation pulse is used.

- **Determined the effect of the physical properties of the sample on the mass of materials ablated.**

Four samples of high purity copper were processed to vary the tensile strength of the samples. Results show that the depth of the crater increases regularly with number of laser pulses and with the tensile strength of the sample at both high and low irradiances. Volumes, and presumably the mass ablated, go through a maximum in samples of intermediate tensile strength. The results of the measurements of crater profiles were presented at the Winter Plasma Conference in January, 2000.

- **Developed and tested methods for alloy identification by LIBS.**

We developed methods to analyze the entire spectrum to quickly identify the class of material such as stainless steel, carbon steel, mild steel, brass.... The identification of class of material based on a single LIBS spectrum is 97.4% accurate, and the correct alloy is identified in 79.9% of the cases. This work has been described in *J. Anal. Atomic Spectrosc.*

- **Developed and tested methods for the determination of RCRA metals in aqueous solutions**

A unique application was developed and tested in which RCRA metals in environmental samples (surface water, ground water, or waste water) were measured by LIBS. The metals in the samples were removed as the samples were either filtered through or placed in contact with chelating membranes. The membranes were dried and analyzed by LIBS allowing fast, rapid, *in situ* analysis of water. Such a system can easily be used in concert with fiber optic elements to provide remove analysis of elemental species. The linearity and limits of detection, combined with the ruggedness, make this method a viable candidate for future development.

Additional Research that Originated from this Grant

After the conclusion of the grant, the science was further developed and applied to other areas and samples. Most of this work was based wholly or in part on the work funded by the Department of Energy.

- **Field-testing for gunshot residues**

After the grant ended, the science was extended to develop a method that could be used as a field portable system to detect the presence of gunshot residue on the hands of a suspected shooter. This work was presented at an international conference and has been published in *Applied Optics*.

- **Additional applications on Dual-Pulse LIBS**

The dual-pulse technique has been extended to measuring the elemental composition of glasses that mimic those produce by the DWPF at the Savannah River Site. The dual-pulse technique obviates the need to dissolve the sample, thus improving turnaround time, and potentially providing a tool for process control.

- **Non-gated detection**

We recently demonstrated excellent LIBS detection for Pb using a non-gated detector. Most previous LIBS measurements have used an expensive, complicated gated detector. Most importantly, the non-gated technique speeds up the analysis time considerably with a 0.1 s measurement This technique works using a fast, 1.3 ps, laser pulse. Turnkey, commercial, fast laser systems are already available and field rugged systems are being developed.

- **Ultrashort pulses in LIBS**

We have developed partnerships with scientists at Lawrence Livermore National Lab and have, for three summers, used their facilities to investigate the applicability and utility of ultrashort pulses to LIBS. The LLNL facility includes a Ti-sapphire laser and amplifiers that provide pulse approximately 100 fs in duration. The work shows clearly that the shorter pulses have far fewer interferences and can provide fast and effective sampling and excitation for samples that are intractable to other methods. This work has been described at a number of conferences and has been the subject of several publications.

Publications Resulting From or Related to this Work

20 publications resulted from the research supported by this grant.

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

"Fiber-optic probe for determining heavy metals in solids based on laser-induced plasmas," B. J. Marquardt, B. M. Cullum, T. J. Shaw and S. M. Angel, *SPIE Proc.*, **3105**, 203-212 (1997).

"A Novel Probe for Laser-Induced Breakdown Spectroscopy and Raman Measurements Using an Imaging Optical Fiber," B. J. Marquardt, D. N. Stratis, D. A. Cremers, and S. M. Angel, *Appl. Spectrosc*., **42**, 1148-1153, (1998).

"Some New Uses for Filtered Fiber-Optic Raman Probes: In *Situ* Drug Identification and *In Situ* and Remote Raman Imaging," S. M. Angel, J. C. Carter, D. N. Stratis, B. J. Marquardt, and W. E. Brewer, "*J. Raman Spectrosc*., **30**, 795-805, (1999).

"Characterization of Laser-Induced Plasmas for Fiber-Optic Probes," D. N. Stratis, and S. M. Angel, *SPIE Environ. Monitoring and Remediation Tech.*, **3534-88**, 592-600, (1999).

"Dual-Pulse LIBS: Why are two lasers better than one?" D. N. Stratis, K. L. Eland, and S. M. Angel, *SPIE Environ. Monitoring and Remediation Tech.*, **3853-61**, (2000).

"Development of a dual-pulse fiber-optic LIBS probe for in-situ elemental analyses," K. L. Eland, D. N. Stratis, J. C. Carter and S. M. Angel, *SPIE Environ. Monitoring and Remediation Tech.*, **3853-42**, (2000).

"Dual-Pulse LIBS Using a Pre-Ablation Spark for Enhanced Ablation and Emission," D. N. Stratis, K. L. Eland and S. M. Angel, Appl. Spectrosc. **54** (2000) 1270-1274.

"Enhancement of Aluminum, Titanium and Iron in Glass Using Pre-Ablation Spark Dual-Pulse LIBS," D. N. Stratis, K. L. Eland and S. M. Angel, Appl. Spectrosc. **54** (2000) 1719-1726.

"Identifying alloys by laser-induced breakdown spectroscopy with a time-resolved high resolution echelle spectrometer," Scott R. Goode, Stephen L. Morgan, Richard Hoskins, and Allison Oxsher, *J. Anal. At. Spectrom.*, **15**, 1133-1138, 2000.

"Energy Dependence of Emission Intensity and Temperature in a LIBS Plasma using Femtosecond Excitation," K. L. Eland, D. N. Stratis, D. M. Gold, S. R. Goode, and S. M. Angel, Appl. Spectrosc. **55** (3), (2001) pp.286-291.

"Some Comparisons of LIBS Measurements Using Nanosecond and Picosecond Laser Pulses," K. L. Eland, D. N. Stratis, T. Lai, M. A. Berg, S. R. Goode, and S. M. Angel, Appl. Spectrosc. **55** (3), (2001) pp. 279-285.

"Effect of Pulse Delay Time on a Pre-ablation Dual-Pulse LIBS Plasma," K. L. Eland, D. N. Stratis, D. M. Gold, S. R. Goode, and S. M. Angel, Appl. Spectrosc. **55** (2001) p.1297-1303.

"LIBS Using Dual- and Ultra-short Laser Pulses," S. M. Angel, D. N. Stratis, K. L. Eland, T. Lai, M. A. Berg, and D. M. Gold, *Fresenius' J. Anal. Chem*., **369** (2001) 320-327.

"Comparison of Acousto-optic and Liquid Crystal Tunable Filters for LIBS," D. N. Stratis, K. L. Eland, J. Chance Carter, S. J. Tomlinson and S. M. Angel, Appl. Spectrosc. **55** (2001) p. 999-1004.

"Analysis of Aqueous Solutions by LIBS of Ion Exchange Membranes," N. E. Schmidt and S. R. Goode, *Appl Spectrosc*. **55** 370-74 2002

"Detecting gunshot residue by laser induced breakdown spectroscopy." Goode, Scott R.; Dockery, Christopher R.; Bachmeyer, Michael F.; Nieuwland, Alexander A.; Morgan, Stephen L. *Trends in Optics and Photonics* (2002), 81(Laser Induced Plasma Spectroscopy and Applications), 175-177.

"Quantitative elemental analysis of metal alloys by laser induced breakdown spectroscopy using multivariate calibration." Goode, Scott R.; Hoskins, Richard; Morgan, Stephen L. *Trends in Optics and Photonics* (2002), 81(Laser Induced Plasma Spectroscopy and Applications), 36-38

"Laser-induced breakdown spectroscopy for the detection of gunshot residues on the hands of a shooter: applicability and analysis of error," Christopher R. Dockery and Scott R. Goode. *Applied Optics* 42(30), 6153-6158, (2003)

"Dual-pulse LIBS using combinations of femtosecond and nanosecond laser pulses," Jon Scaffidi, Jack Pender, Bill Pearman, Scott R. Goode, Bill. W. Colston, Jr., J. Chance Carter, and S. Michael Angel, Applied *Optics*, 42(30), 6099-6106, 2003.

Graduate Education Resulting from this Work

Ph.D. Dissertations

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

Dimitra Stratis "Characterization of dual-pulse laser-induced breakdown spectroscopy for the analysis of solid materials." August 2000

Kristine Eland "Laser-induced breakdown spectroscopy using ultrashort and dual pulses." 2001.

Andrea A. Thomas, "Calibration, Optimization and Discrimination for Metals Analysis Using Atomic Absorption and Laser Induced Breakdown Spectroscopy." December 2002

Allison M. Oxsher, "Characterization of Matrix Effects and Spectral Discrimination in Laser-Induced Breakdown Spectroscopy of Solid Samples." December 2002

M.S. Thesis

Mary Peyton Davis, "The Determination of Carbon in Steel by Laser Ablation into a Microwave-Induced Plasma," 1999.

Conference Papers Resulting from this Work

The results of research supported by this grant were given in 34 Conference presentations.

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).

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).

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).

“Laser Ablation as a Technique for the Introduction of Solid Polymer Samples Into a Flame,” Brian Cullum, Brian Marquardt and S. Michael Angel, The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, Georgia, March 16-21, Abstract **906** (1997).

FACSS, Vancouver BC. (LIBS Symposium) "Fundamental Studies of Laser-Induced Breakdown Spectroscopy." Invited. November 1998

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).

"Optimization of Laser Parameters for Dual-Pulse LIBS," Dimitra N. Stratis, Kristine L. Eland and S. Michael Angel, presented at 25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Paper **583**, Austin, TX, October 11-15, 1998.

"Wavelength Optimization for Fiber-optic LIBS," Dimitra N. Stratis, Kristine L. Eland and S. Michael Angel. presented at 25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Paper **707**, Austin, TX, October 11-15, 1998.

"Factors influencing selective volatilization in laser induced breakdown spectroscopy (LIBS), with Mary Peyton Davis, Allison Oxsher, and Richard Hoskins, Pittcon-99, March, 1999, Orlando FL.

“Characterization and Optimization of Laser Parameters for Dual-Pulse LIBS,” D.N. Stratis, K.L. Eland, and S.M. Angel, Paper #880, Pittsburgh Conference and Exposition, Orlando, FL, March 10, 1999.

“A Comparison of Acousto-optic and Liquid Crystal Tunable Filters for Time-Resolved Plasma Imaging,” D.N. Stratis, K.L. Eland, and S.M. Angel, Paper #35, Pittsburgh Conference and Exposition, Orlando, FL, March 8, 1999.

“Optimization of Wavelength for Remote Fiber-Optic LIBS Measurements,” K.L. Eland, D.N. Stratis, and S.M. Angel, Paper #878, Pittsburgh Conference and Exposition, Orlando, FL, March 10, 1999.

“Design and Evaluation of Fiber-optic LIBS Probes Using Dual Laser Pulses,” Kristine L. Eland, Dimitra N. Stratis and S. Michael Angel, Pittsburgh Conference, New Orleans, LA March 2000.

“Factors Affecting Enhanced LIBS Signals Following Dual-Pulse Excitation,” Dimitra N. Stratis, Kristine L. Eland, and S. Michael Angel, Pittsburgh Conference, New Orleans, LA March 2000, paper No. 953.

"Laser-Induced Breakdown Spectroscopy with a Time-Resolved High Resolution Spectrometer" - Scott Goode, Richard Hoskins, Pittcon 2000, March, 2000

"Analysis of Laser-induced breakdown spectroscopy at very short times," FACSS, Nashville, TN October 2000, with Richard Hoskins

"Optimization of parameters in laser induced breakdown spectroscopy," FACSS, Nashville, TN October 2000, with Andrea Thomas

"Use of LIBS to Identify Ammunition." Invited presentation American Chemical Society Southeastern Regional Meeting, 2000

"Discrimination of ammunition fragments using laser induced breakdown spectroscopy and canonical variate analysis," Poster paper presented at the Southeast Association of Academic Analytical Chemists (SEAAC), Columbia, SC 2 November 2001.

"Laser Induced Breakdown Spectroscopy of Ion Exchange Membranes to Determine the Elemental Composition of Solutions," Norman Schmidt and Scott R. Goode, Pittcon 2001

"Fundamental Studies of Laser Induced Breakdown Spectroscopy at Short Times," Richard Hoskins, Scott R. Goode, Pittcon 2001

"Using Response Surfaces to Evaluate Interactions Between Instrumental Parameters in Laser Induced breakdown Spectroscopy," Andrea Thomas and Scott R. Goode, Pittcon 2001.

"Effects of Noise on Alloy Identification by Laser Induced Breakdown Spectroscopy," Allison Oxsher and Scott R. Goode, Pittcon 2001.

"LIBS Using Dual- and Ultra-Short Laser Pulses," S. Michael Angel, Scott R. Goode, Dimitra Stratis, Kristine Eland, Tianshu Lai, Mark Berg, and Dave Gold, Pittcon 2001.

"LIBS Using Dual-and Ultra-Short Laser Pulses," S. Michael Angel, Scott R. Goode, Dimitra N. Stratis, Kristine L. Eland, Tianshu Lai, Mark A. Berg, and David M. Gold, paper 2001P, PITTCON 2001, New Orleans, LA March 4-9 (2001).

"A Comparison of Ultra-short and Nanosecond Laser Pulses for LIBS," Kristine L. Eland, Dimitra N. Stratis, S. Michael Angel, Mark A. Berg, and David M. Gold, paper 1398, PITTCON 2001, New Orleans, LA March 4-9 (2001).

"Pre-Ablation Spark Dual-Pulse LIBS," Kristine L. Eland, Dimitra N. Stratis, and S. Michael Angel, paper 1399, PITTCON 2001, New Orleans, LA March 4-9 (2001).

Patent Disclosures

Three inventions were disclosed as a result of research supported by this grant.

Disclosure title: "On-Site Determination of Lead in Paint Using a Novel Optical Fiber Probe." Disclosure #00129.

Disclosure title: "Enhanced Laser Ablation and Enhanced Laser-Induced Breakdown Emission Using Dual-Pulse Excitation:" Disclosure #00235.

Disclosure title: "On-Axis Fiber-Optic Pre-Ablation Spark Dual-Pulse LIBS Probe:" Disclosure # 00301.