

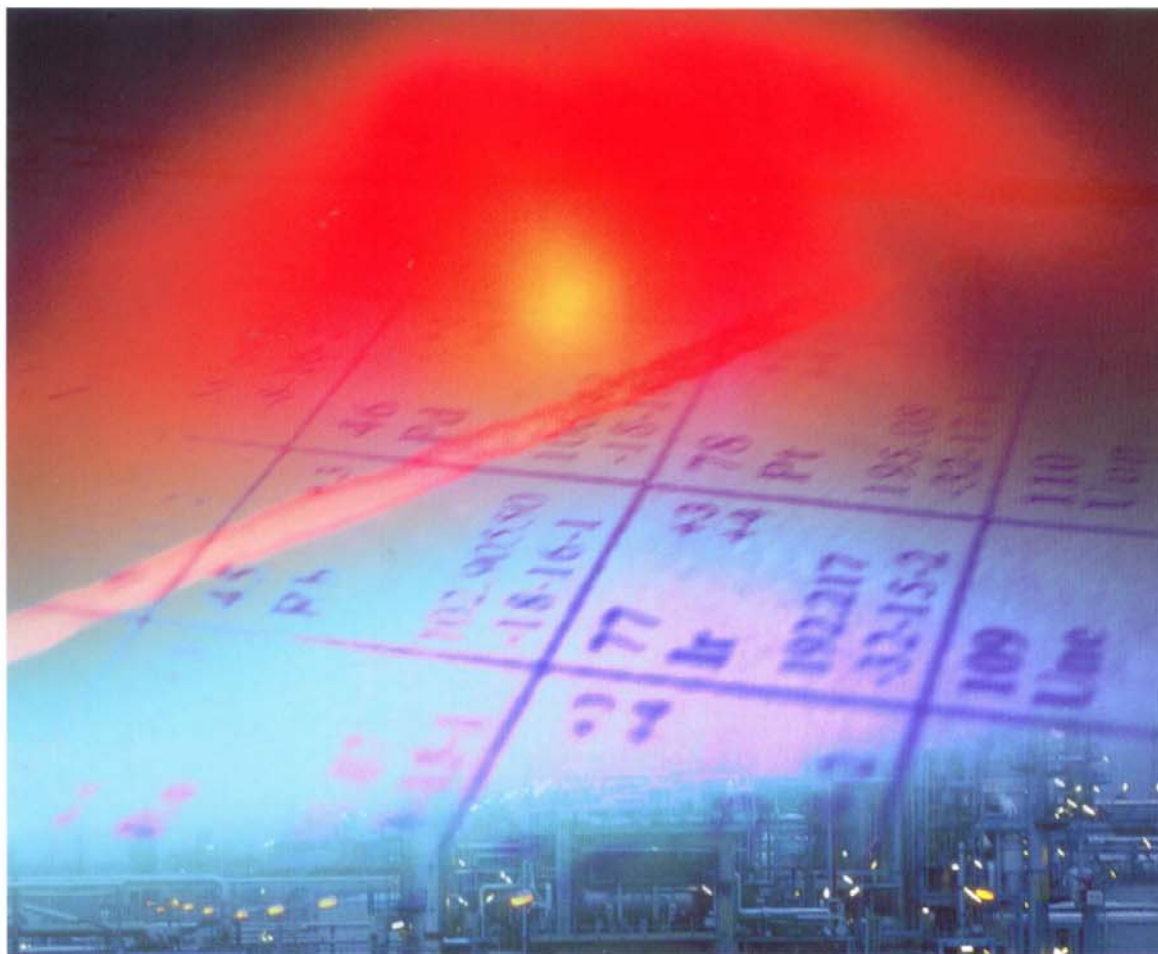
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Lasers in Chemistry

Probing Matter

Volume 1



Laser Induced Breakdown Spectroscopy (LIBS)

Michael J. Myers, John D. Myers, Abbey G. Myers
Kigre, Inc., 100 Marshland Road, Hilton Head Island, SC 29926
Ph# 843-681-5800, E-mail: kigreinc@cs.com

1 Introduction

LIBS (laser induced breakdown spectroscopy) is a relatively new version of atomic emission spectroscopy made possible with the invention of the laser. A high-energy laser pulse is focused down to target a gas, liquid, or solid substance creating a dielectric breakdown or “plasma spark”. This high-temperature atomization provides sufficient energy to transition atoms into distinct atomic energy levels. The atoms then decay resulting in narrow “fingerprint” elemental emission line spectra. LIBS is similar to other analytical methods such as flame emission, ICP (inductively coupled plasma), direct-current plasma and microwave-induced plasma spectroscopy.

The integration of laptop computers, miniature fiber optic spectrometers and small high power laser transmitters has led to the development of portable LIBS analytical equipment. LIBS portable analyzer systems are capable of real-time qualitative & quantitative in-situ analysis with little or no sample preparation. The capability to perform in-situ chemical analysis in the field with instant results using a small, man portable, battery operated device is appealing. This capability has captured the imagination of scientists and engineers who have initiated research and development into a host of new LIBS applications and techniques.

2 Basic principles & history of laser plasma spectroscopy

Emission line spectroscopy is based upon "quantum" theory and was proposed over 140 years ago [1]. LIPS (laser plasma spectroscopy) also known as Laser Induced Breakdown Spectroscopy (LIBS), is a relatively new type of atomic emission line spectroscopy made possible with the advent of the laser in 1961[2]. LIBS was originally coined by Leon Radziemski and David Cremers at LANL (Los Alamos National Laboratory) in New Mexico (USA) in 1981 [3]. In the age of computer search engines, it became apparent that LIPS had too many alternative meanings outside the field of analytical spectroscopy. Therefore, LIBS has become the preferred acronym instead of LIPS for laser plasma spectroscopy. The LIBS designation was further promoted as an international standardized acronym for laser plasma spectroscopy by Andrzej Miziolek ARL (U.S. Army Research Labs) during the first international LIBS conference held in Tirrenia, Pisa (Italy) in 2000 [4].

In the early 1960's Lloyd Cross of Trion Instruments (Ann Arbor, MI, USA) and Fred Brech of Jarrell-Ash Company (Waltham, MA, USA) developed the first LIBS atomic line spectroscopy system. The initial "MARK I Optical Microprobe" device utilized the "third" ruby laser ever built and became the first commercially available analytical instrument to use a laser [5,6]. For more information, the reader is referred to chapter [p3]. The MARK I was arranged so that a Q-switched ruby laser pulse (~ 0.4 joule @ 694 nm red) was focused down onto the sample surface, ablating the sample and creating a vapor of the material. The vaporized material was subsequently ionized between high voltage electrodes. The ionized sample emission was then spectrographically collected and measured on photographic plates as atomic line intensities [7,8]. Following the MARK I, the MARK II employed a Q-switched neodymium glass laser demonstrated by John Myers of Lear-Sigler Systems Center, (Ann Arbor, MI USA). Lear-Sigler purchased Trion Instruments in 1962. The MARK II Nd:glass laser proved to be less temperature sensitive and it provided higher pulse energies than the MARK I Ruby laser. It provided more than 0.5 joules @ 1062nm in the

near infrared, NIR creating a higher power density plasma and better signal to noise ratio [9].

Early Q-switched ruby and Nd:glass laser systems were used to evaluate various laser-material interactions. These included the power density effects in laser produced craters, the thrust producing capabilities of lasers and the evaluation of the laser's potential use in directed energy weapons and nuclear fusion reactors [10, 11]. For more information, the reader is referred to chapter [p37]. During the 1980's, Neodymium doped Yttrium Aluminum Garnet (Nd:YAG) lasers became the most common laser system used in most applications including LIBS. Nd:YAG crystal laser became popular for LIBS because they were easily configured to produce the megawatt peak power levels required for reliable laser plasma generation. During the 1980's and 1990's the relatively high expense and large size associated with lasers and spectrophotometers insured that Ion Conductive Plasma and other laboratory instruments remained more attractive for most commercial chemical analysis applications.

A number of portable LIBS systems were developed for field-testing environments during the 1990s. One example is a US Army LIBS sensor for subsurface in-situ soil classification and heavy metal contamination detection. This system is part of the SCAPS (site characterization analysis penetrometer system) The cone penetrometer system consists of a steel cone that is hydraulically pushed into the ground while in-situ measurements are continuously collected and transported to the surface for data interpretation and visualization. The U.S. Army Engineer Waterways Experiment Station field-portable LIBS system included a rugged compact (1.25" diameter x 14" long) 17-Megawatt Nd:YAG laser probe and fiber-optic delivery system [12,13]. The system's remote LIBS probe was lowered into deep wells and used to measure trace amounts of heavy metals contaminants in soil and water. Scientists at LANL, developed portable LIBS systems for the determination of metals in soils that led to LIBS for use on Mars Rover missions [14,15,16,17]. The Mars Rover LIBS system is shown in figure 2.10. This became an important development for the National Aeronautic Space

Comment: Figure 2.10 reference

Administration (NASA). A thin dust layer covers everything on the Martian surface. It was found that the Mars Rover x-ray analysis system was not able to provide chemical composition data on underlying Martian rock and soil. LANL developed space qualified portable LIBS technology for NASA in order to penetrate the coated Martian surface. This LIBS system is expected to provide an extremely versatile and portable method of determining the elemental composition of Martian gases, liquids, and solids on future space missions.

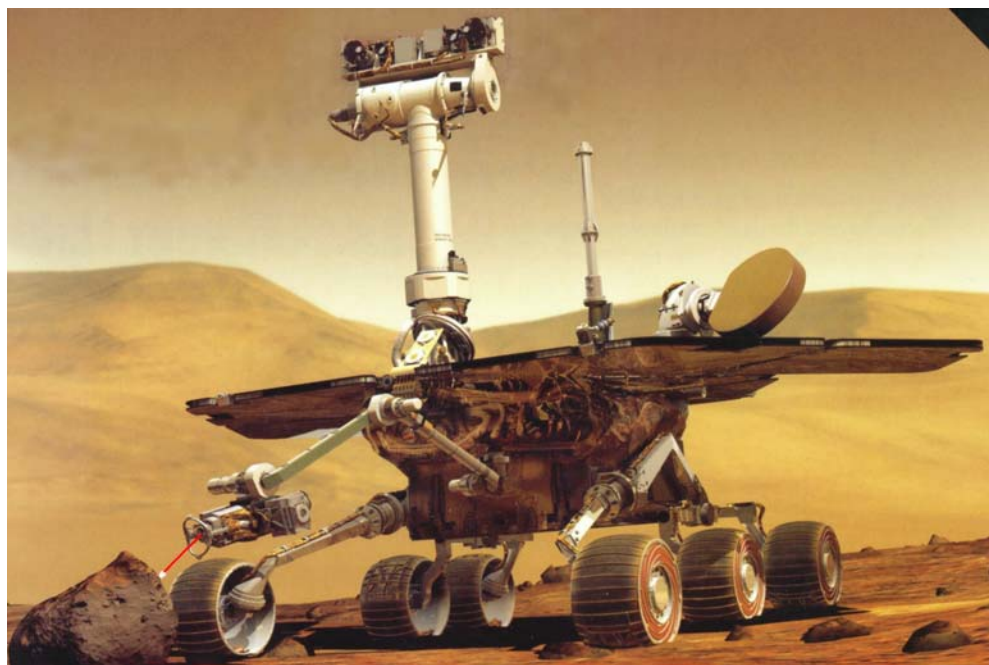


Figure 2.10 Illustration of the Mars Rover LIBS system method for determining the elemental composition of Martian gases, liquids, and solids.

After 2001, Homeland Security and the war on terror sparked interest in LIBS as a promising portable technology for detecting explosives, landmines, biological weapons and chemical contamination [18]. LIBS studies at ARL (U.S Army Research Labs) during the 1990s led to the development of portable backpack-based LIBS systems for field measurements of potentially hazardous substances and devices [19,20,21,22,23].

Portable LIBS chemical analysis also provides many advantages for use in field-testing for environmental pollutants. The advantages of LIBS include rapid, reliable, multi-elemental in-situ analysis with little or no sample preparation.

The integration of miniature fiber optic spectrometers with small high peak power laser transmitters lead to the development of compact portable analytical equipment assembled with commercial “off-the-shelf” components. In a typical modern LIBS system, a high peak power pulsed 1064nm Nd:YAG laser is focused to produce a plasma on a targeted material. For more information, the reader is referred to chapter [p31]. Elemental line spectra is created, collected and analyzed for the elements present. LIBS analysis data is processed and displayed with nearly instantaneous speed on laptop computers. A schematic of a modern LIBS system is shown in figure 2.20. It is comprised of the following basic elements:

Comment: Figure 2.20 reference

- 1) *A high peak power Q-switched laser output (~1-50 ns pulse width)
- 2) Delivery optics to focus the laser pulse onto the target surface
- 3) Laser pulse emission and detection timing circuitry
- 4) Optics to gather plasma emission and transfer to the spectrometer
- 5) A spectrophotometer to separate the emission line spectra
- 6) A computer for wavelength analysis of the emission line spectra

* Note: A Q-switch is a device that is similar to a shutter that controls the laser resonator's ability to oscillate. This shutter effect allows one to spoil the resonator's "Q-factor," keeping it low to prevent lasing action. Under these conditions, the laser gain material is able to store higher levels of energy. The extra stored energy is subsequently extracted as laser light emission in the form of extremely short pulse width, high-peak-power pulses.

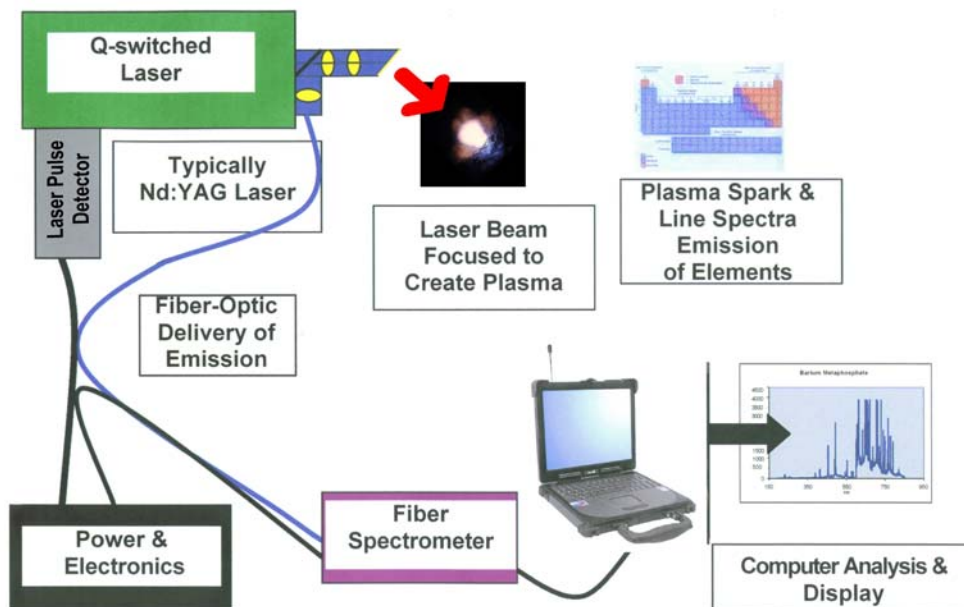


Figure 2.20 A schematic of a modern LIBS system including laser, delivery optics, signal collection optics, spectrophotometer and computer.

3 Laser plasma generation

3.1 Detector Timing & Multiple Pulse LIBS

The optimization of LIBS system event timing is important for efficient capture of high resolution line spectra. During the first microseconds after the focused laser pulse initiates a plasma “spark”, the resulting plasma energy is dominated by a strong “white light” continuum also described as broadband black body or bremsstrahlung radiation emission. Bremsstrahlung is from the German *bremsen*, to brake and *strahlung*, radiation, thus, "braking radiation" or "deceleration radiation". This is essentially electromagnetic radiation that is produced by the acceleration and collision of charged particles (read electrons) with other charged particles such as atomic nuclei [3,24].

The initial few microsecond after plasma ignition is followed by a longer period when elemental line spectra emission shows up as the dominating broadband emission decays. For more information, the reader is referred to chapter [p39]. The optimum “gate” time for turning on the spectrometer, and avoiding the masking broadband bremsstrahlung emission, is typically one or two microseconds after the plasma initiation. For electro-optic Q-switched lasers, the Q-switch timing electronics are used to establish a T_0 laser/plasma ignition mark. For passive or saturable absorber Q-switched lasers a photo-diode is required to “pickoff” the laser output as a T_0 laser/plasma ignition timing mark. In either case, the T_0 is used to start the system electronics clock and set a spectrophotometer gate. Figure 3.10 shows an event timeline for a typical single pulse LIBS system.

Comment: Figure 3.10 reference

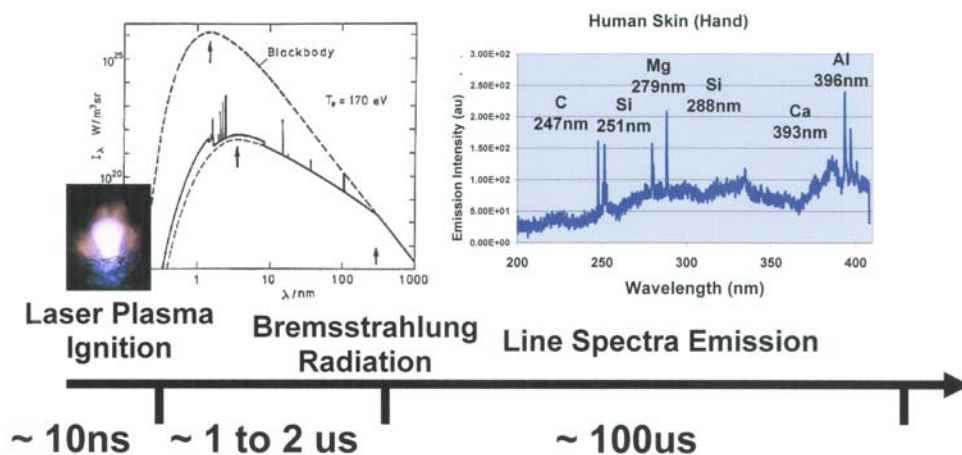


Figure 3.10 LIBS dominant radiation emission event timeline starting with the laser plasma ignition.

Multiple pulse laser operation may be used to enhance line spectra detection by pumping additional energy, via additional focused laser pulses, into the plasma envelope before the emission decay of the proceeding pulse is completed. The laser is adjusted so as to introduce a number of Q-switched pulses in a “pulse train” output. The initial laser pulse is followed by additional pulses with microseconds time duration in between. For example the laser may produce three separate pulses each 4 ns pulse duration, 20 mJ

energy and with 25 μ s between each pulse. The first pulse initiates the plasma on the sample surface and the second and third pulses feed more energy into the plasma causing the plasma to expand. The net result is higher energy plasma and a better signal to noise ratio for the captured line spectra. An example of single, double and triple pulse LIBS nickel metal spectra was provided by Will Pierce and Ryan Slaherty of StellarNet, Inc. [25] and shown in figure 3.20.

Comment: Figure3.20 reference

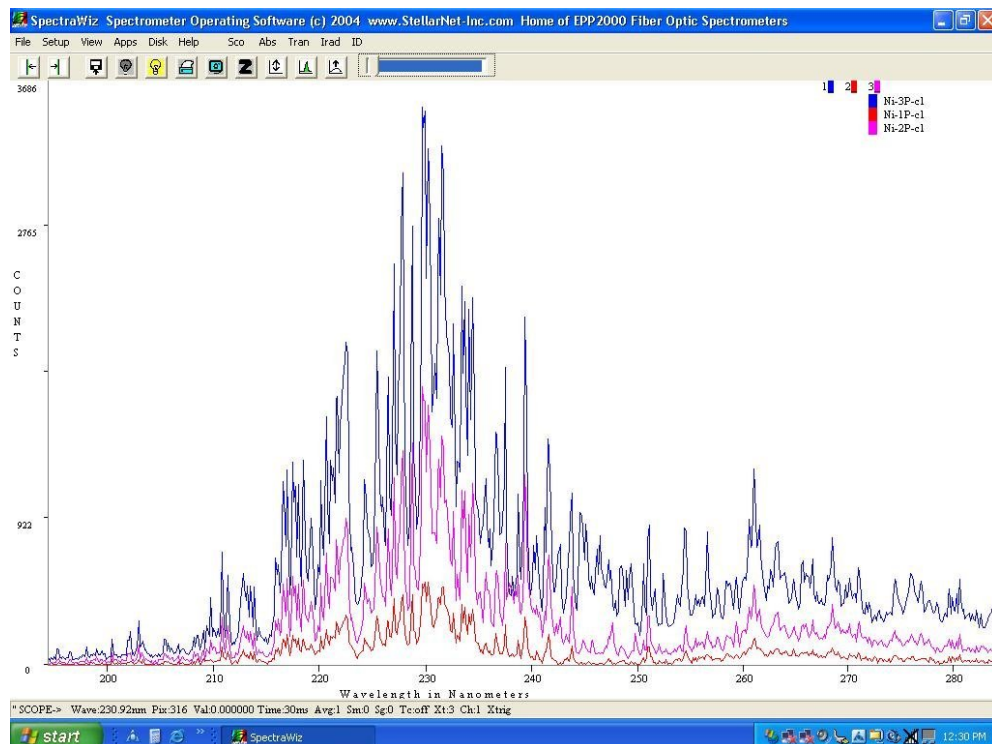


Figure 3.20 Comparison of the signal-to-noise ratio for single (1/1), double (2/1) and triple (3/1) pulse LIBS spectra centered on a strong 231nm emission line for nickel [25]

3.2 Laser material interaction

The LIBS system laser beam is typically focused down to the smallest possible spot size as dictated by the beam's quality and the design of launch/conditioning optics. The laser pulse impacts the targeted material which causes an induced electric breakdown

or avalanche ionization. This process assumes that the breakdown threshold is reached in terms of sufficient laser energy density and peak power density. A fundamental breakdown threshold is characteristic for each type of material under given environment conditions [26]. Materials exhibiting a strong absorption at the laser wavelength will initially exhibit strong surface ablation which provides for lower breakdown thresholds. The use of higher energy shorter wavelength laser radiation has been shown to significantly reduce breakdown thresholds via a resonance-enhanced two-photon ionization process [27]. For more information, the reader is referred to chapter [p9]. In general, materials transparent to the laser wavelength will exhibit higher breakdown thresholds. For applications involving solids, liquids and gases a relatively simple “short” focal length lens system may be employed with modest laser power densities levels to perform LIBS experiments. Longer standoff, LIBS systems typically require more complicated optical delivery systems and higher peak power laser pulses for effective performance.

Laser plasma formation in air or gas requires at least one electron in the focal region when the laser pulse arrives. While in most cases this is probability very high, the thresholds for gas and air breakdown are found to be much higher than that of liquids and solids. Laser induced breakdown formation in gas and air is inhibited at lower pressures and enhanced at higher pressures. Xenon and heavier gases exhibit low thresholds while lighter gasses such as helium exhibit breakdown thresholds orders of magnitude higher [28].

3.3 Power density, pulse width and color temperature

Plasma temperature has been shown experimentally to be proportional to the peak laser power [29,30]. Lasers often used for LIBS applications produce peak power densities in the range ~ 0.5 to 100 megawatts. These power densities produce plasmas exhibiting initial ionic and electron temperatures ranging from approximately 5,000 to greater than 20,000 K (0.5 to 8.6 eV) [3,4,27,31]. Bremsstrahlung emission decay times of ~ 1-2 μ s as illustrated in figure 2.1 are associated with nanosecond pulse width lasers

that typically produce initial plasma color temperatures greater than 14,000K. Short femtosecond or picosecond laser excitation pulse widths produce plasma with 10x faster bremsstrahlung continuum emission decay times. As a result of the shorter broadband background emission duration, ultra-short pulse LIBS allow for more efficient capture of fine line emission spectra often without the need for gated detectors [30,32].

4 Qualitative analysis

4.1 Emission line analysis

Qualitative chemical analysis with LIBS begins with the identification of the stronger emission lines provided by LIBS spectra. In addition, one may also search out a material's LIBS spectra for the presence of specific lines associated with elements of critical interest. Numerous references for atomic line spectra wavelength and relative intensity are found in the general literature. ARL and the NIST (U. S. National Institute of Standards and Technology) provide line spectra public data bases on the World Wide Web [33,34]. These web sites include reliable LIBS research tools that are informative and easy to utilize. The ARL site includes only the stronger emission lines for approximately 72 elements referenced from LIBS technical publications. The NIST site is more comprehensive and compiles both weak and strong emission lines for over 100 elements referenced from various atomic line emission spectroscopy references. Many commercial fiber spectrophotometer manufactures now include extensive atomic line spectra libraries and automatic line identification software as part of their standard computer spectra display software. Wavelength resolutions of 0.03nm to 0.2nm are common and often adequate for identification of a major element by a strong line emission.

Positive identification of an element is readily verified by the presence of at least 2 strong to moderate intensity lines. For example, Cu^+ exhibits two strong emission lines that reside near each other in the UV part of the spectrum at 324.754nm and 327.396nm and approximately 60 lines of moderate strength in the 200 to 800nm region. Copper metal foil line spectra, as shown in figure 4.1, may be used as a line identification

Comment: Figure 4.10 reference

reference standard. It is also useful as a check on the wavelength calibration of the system spectrophotometer. The ratio of line intensity of the two distinct spectral lines adds another characteristic property useful in LIBS qualitative analysis efforts. Organic materials are typically identified with a “fingerprint” intensity of multiple lines related to the relative concentrations of carbon, oxygen, nitrogen and hydrogen. Example “fingerprint” LIBS for anthrax is shown in figure 4.11 [34].

Comment: Figure 4.11 reference

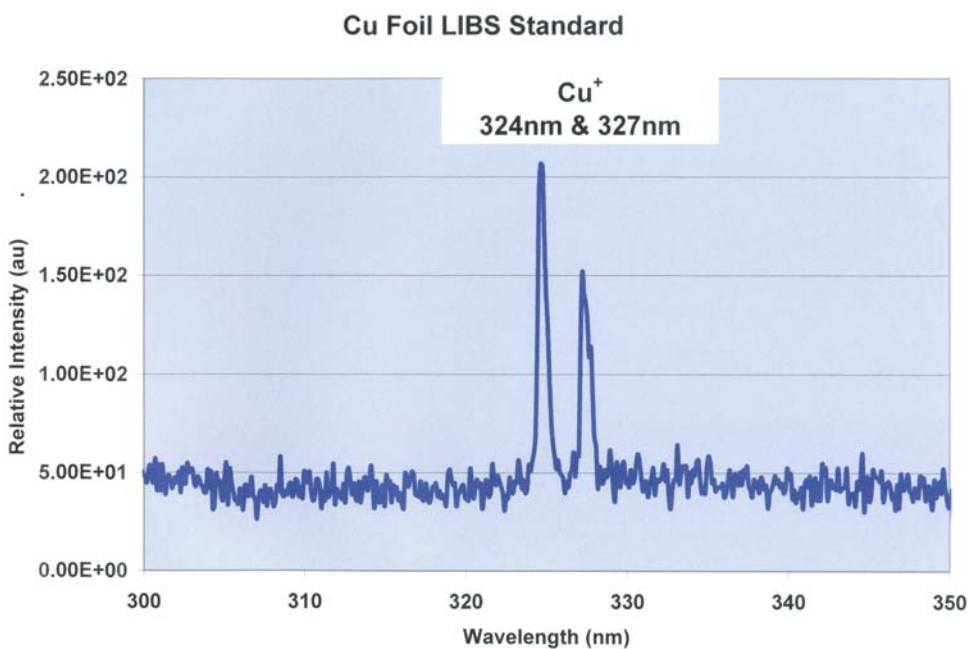


Figure 4.10 Copper foil LIBS spectra reference standard

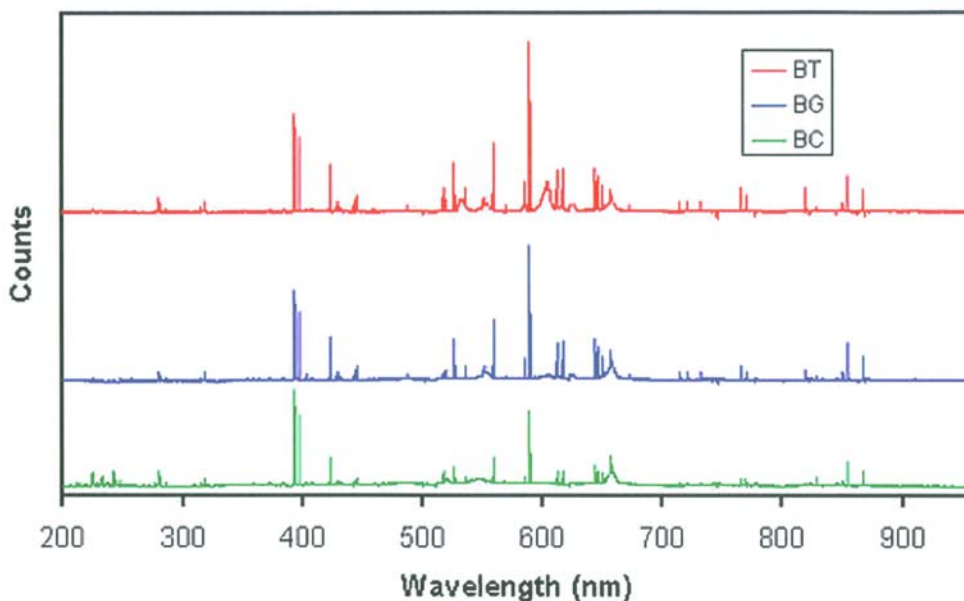


Figure 4.11 Anthrax fingerprint LIBS spectra, BT (Bacilli Thuringiensis), BG (Bacilli Globigii) and BC (Bacilli Cereus) [34]

4.2 Host influence on emission line spectra and detection limits

Adverse affects from the environment and/or chemical composition of the targeted sample may affect the intensity of the emission line in an unpredictable manner. The effect of host elements on the analyte during in a LIBS plasma reaction is known as a matrix effect. Matrix effects are an adverse host influence on LIBS resulting in inconsistent line spectra intensity due to chemical composition and material properties. With each laser shot on a given targeted material the substance under study is changed via reactions with its surroundings. Plasma-material interaction is influenced by the sample's composition, atmosphere, surface conditions and optical properties. Materials exhibiting a uniform hard solid surface tend to exhibit lower spectral matrix effects then when compared to softer non-uniform granular or powdered materials. Soil and sediment samples tend to be especially susceptible to matrix effects. Successive LIBS plasma shots of soil produce a micro-environment mixture of quenched molten minerals and organics. The soil emission lines from the plasma are changed by the heating and cooling process. The elements may become oxidized or reduced as they are encapsulated in

either an amorphous or crystalline environment. For more information, the reader is referred to chapter [p48]. Spectral line masking and shot-to-shot instability may also be the result from physical ejection of granular particles more prevalent in ablation of fine powder samples. In general, obtaining predictable and repeatable line spectra becomes more difficult when the line spectra of interest are partially or completely blocked due to matrix effects [35,36]. Methods used to mitigate matrix effects in LIBS are discussed in the quantitative analysis section.

The detection limits for elements analyzed via LIBS technique are typically found to be in the ppm (parts per million) range. Detection limit values are influenced by matrix effects, instrumentation, environment and measurement parameters. Temporal gating optimization has been shown to lower the detection limit and enhance the signal to noise ratio for line intensities associated with given elements of interest [37]. In the Fisher study cadmium, mercury and arsenic exhibited high signal to noise ratio line emissions with a 2-10 μs gate time while lead and chromium line emissions peak intensities were enhanced using a 20-40 μs time delay. An example LIBS spectra showing enhancement of line intensity with gate time adjustment is shown in figure 4.20 [25]. Literature survey compilations of LIBS and ICP detection limit values for various elements and conditions are available from a number of commercial and academic sources [3,34,38,39].

Comment: Figure 4.20 reference

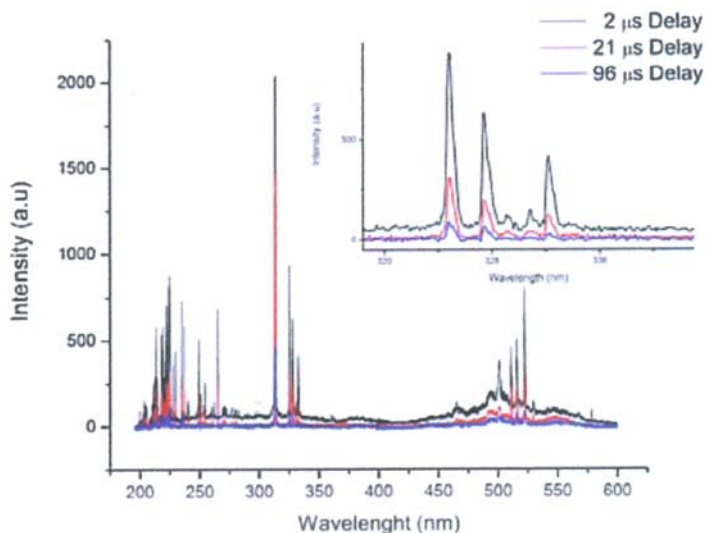


Figure 4.20 LIBS element line intensity enhancement with spectrophotometer gate time adjustment [25]

5 Quantitative analysis

5.1 Software calibration techniques

LIBS computer operating software is typically used to setup and control the operation of the spectrophotometer. LIBS spectrophotometer computer software typically includes mathematical algorithms that automatically identify, compare and contrast spectroscopic data. An example of LIBS spectroscopic line identification software is shown in figure 5.10.

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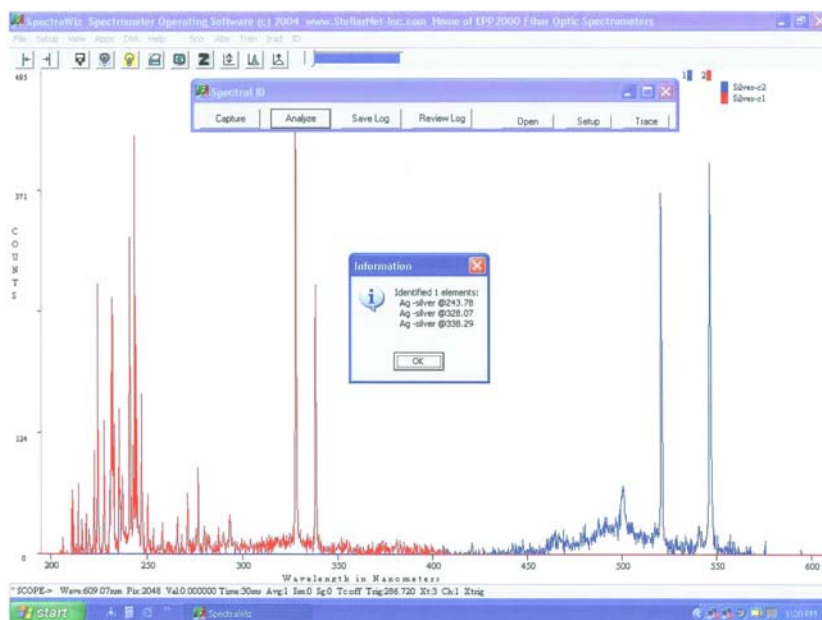


Figure 5.10 StellarNet SpectraWiz LIBS element identification software [25]

Quantitative data may be processed and compared against element concentration standards installed into custom software applications [25,40]. Stored computer library data may include a “standard addition analysis” element concentration line spectra data base. This type of data base may be used in the same manner as that used in “wet” chemistry spectral quantitative analysis. The computer software compares elements with matched line spectra and then applies the relative line intensities in order to estimate the concentration. Reliable quantitative analysis requires calibration curves that include similar matrix effects as the material under investigation [41]. For quasi-quantitative data calibration, standard concentrations and relative line intensity data may be provided from test sample mixtures with additions of known pure metal, salt or oxide samples. In the field, an unknown sample may be standardized by mixing it with sodium borate and fusing it into a glass bead using a small gas torch and platinum crucible. Multiple glass beads may be made from the same unknown material with pre-measured additions of known material to provide accurate standard addition quantitative analysis. The formation of the glass bead negates the matrix effects, normalizes oxidation state changes and eliminates variable host influences on the unknown element. Enhanced semi-quantitative elemental analysis in soils and marine sediments has been shown to benefit from “pellet press” field sample preparation techniques that reduce matrix effects and optimize measurement reproducibility [42]. A sample is mechanically compacted by a small press before insertion into a LIBS sample chamber. Quantitative analysis accuracy and reproducibility of LIBS techniques may be enhanced by recording only the first few laser shots and moving to another spot of the targeted material before recording additional shots [43].

5.2 Neighbor peak ratio comparison

Another type of quasi-quantitative analysis with LIBS involves the observation of the line intensity of neighboring peaks. The line intensity will change with the relative concentration of either two different elements or different oxidation states of the same element. The oxidation state is typically maintained after ablation under normal atmospheric conditions. This method is particularly useful in field analysis with LIBS.

In-situ sample evaluations can be quickly gathered and preliminarily “tagged” for further characterized with reference to location and the relative abundance of a given element or element oxidation state [25]. Example LIBS spectra demonstrating relative line intensity of neighbor element concentrations for iron, copper and arsenic in contaminated and non-contaminated watershed site soil samples are shown in figure 5.20.

Comment: Figure5.20 reference

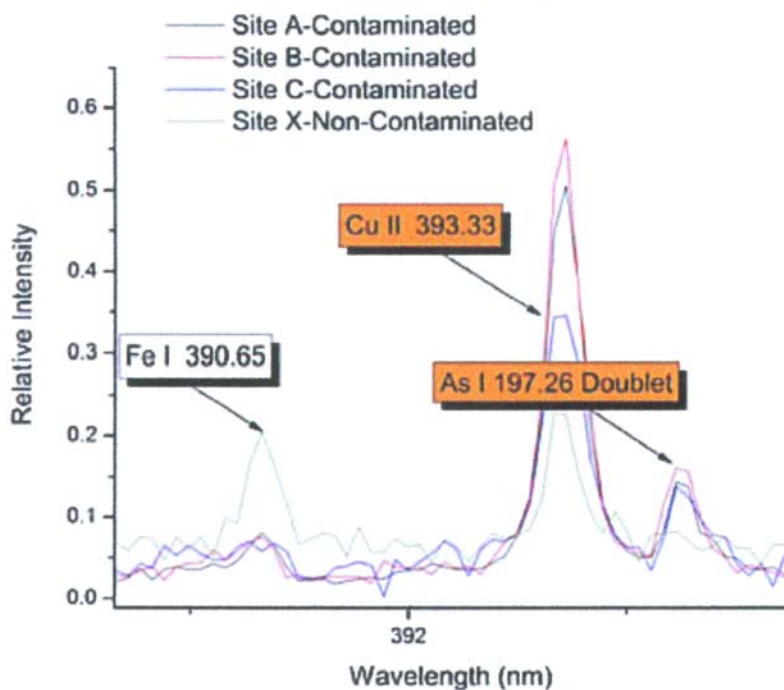


Figure 5.20 LIBS spectra display of relative concentrations of iron, copper and arsenic found in various contaminated and non-contaminated soil samples [25]

6 Applications

LIBS analytical techniques may be practiced with minimal sample preparation and in some cases in-situ. Field-deployable LIBS instrumentation may be configured to provide complete chemical analysis (elemental and compositional) of materials at close, stand-off, and remote distances. Other elemental analytical techniques such as ICP or ICPMS (inductively coupled plasma mass spectroscopy) involve the use of larger

complicated mechanical devices and require laboratory conditions and careful sample preparation. LIBS satisfies the demand for user-friendly, field-portable instruments.

Example applications of LIBS include the following:

Geology (analysis of soils and minerals for mining, oil exploration and construction) [8,9,12,13,15,16,17,25,41,42,44]

Space Exploration (analyzing specific conditions on Mars and Venus to understand their elemental composition) [14, 16]

Environmental Monitoring (real-time analysis of air and water quality, control of industrial sewage and exhaust gas emissions) [12,13,14,15,16,19,25,37,39,41,45, 46,59,61,63,64].

Medical (biological sampling, non-invasive analysis of human hair and teeth for metal poisoning, cancer tissue diagnosis, bacteria type detection, detection of bio-aerosols and bio-hazards, anthrax, airborne infectious disease, viruses, sources of allergy, fungal spores, pollen) [4,47,48,49]. For more information, the reader is referred to chapter [p50].

Archeology (analysis of artifacts, restoration quality) [4,50,51,52]. For more information, the reader is referred to chapter [p51].

Military (detection of biological weapons, explosives, backpack-based detection systems for homeland security) [4,18,21,22,23,53,54,55].

Forensics (evidence in legal proceedings) [56,57,58]

Industrial (in-situ materials composition and processing, contamination identification) [23,36,60,62,65]

7 Outlook & Summary

The development of new laser sources and compact instrumentation is helping LIBS chemical analysis find additional niche markets in everything from environmental monitoring and materials analysis to homeland security, medical diagnostics and space-based research [23]. The advent of new core technologies allows for further design and manufacturing advances in portable LIBS systems that continue to become smaller and less expensive than their predecessors. The attractive capability of real-time in-situ material analysis without sample preparation bodes well for the future of LIBS. New

generation of compact DPSS (diode pumped solid state) HESP (high efficiency side pumped) Q-switched “Eye-safe” Class I lasers provides for practical in-situ LIBS field applications without the need for eye-protection goggles or plasma safety shields. Class I LIBS system eye safety rating is possible through the use of Megawatt peak power Q-switched lasers operating in the narrow spectral window between 1.5 μ m and 1.6 μ m. These lasers are approximately 8000 times more “eye-safe” than other laser devices operating in the visible and near infrared wavelengths [67]. For more information, the reader is referred to chapter [p4]. A picture of a megawatt peak power class I eye-safe high efficiency side pumped diode pumped solid state laser is shown in figure 7.0. For more information, the reader is referred to chapter [p3].

Comment: Figure 7.0 reference

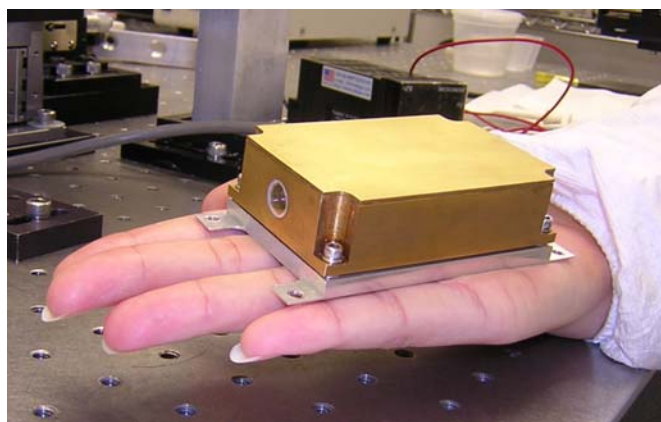


Figure 7.0 Megawatt power Class I eye-safe DPSS HESP erbium glass laser [68]

Further development of smaller low cost high performance fiber spectrophotometers, compact computer systems and advanced software appears to continue. Further customization of LIBS software mathematical algorithms is expected to allow future LIBS systems to become more versatile and user friendly with increased performance and reduced prices.

8 References

- [1] G. Kirchoff and R.W. Bunsen declare that elements have both characteristic absorption and emission spectra. 1859.
- [2] T. H. Maiman, "Stimulated optical radiation in ruby masers", *Nature*, vol. 187, pp. 493-494, August 1960.
- [3] D. Cremers, L. Radziemski, "Handbook of Laser-Induced Breakdown Spectroscopy", John Wiley & Sons, Ltd., 2006.
- [4] A. Miziolek, V. Palleschi, I. Schechter, "Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications", Cambridge University Press, 2006.
- [5] Private communications with Lloyd G. Cross (Gualala, CA, USA), and John, D. Myers (Kigre, Inc. Hilton Head Island, SC, USA) July 2007.
- [6] F. Brech, L. Cross, "Optical Microemission Stimulated by a Ruby MASER", *Applied Spectroscopy*, 16: 59, 1962.
- [7] F. Lytle, "Twenty Years of Laser Research in Analytical Chemistry", *Analytical Chemistry*, pp. 477 A-482 A, July, 2000.
- [8] K. Snetsinger, K. Keil, "Microspectrochemical Analysis of Minerals with the Laser Microprobe", *The American Mineralogist*, Vol. 52, Nov.-Dec., 1967.
- [9] W. Blackburn, J. Schwendeman, "Trace-Element Substitution in Galena" *Canadian Mineralogist*, Vol. 15, pp. 365-373, 1977.
- [10] J. Myers, "Power Density Effects in Laser Produced Craters", Cornell Aeronautical Laboratories, Applied Physics Department, Report File: C27-011, Jan. 27, 1964.
- [11] J. Myers, "RGI/PPI High Power Laser Investigation," Contract N00014-66-C0157, Lear Siegler, Laser Systems Center, July 1, 1966- Feb. 1, 1967.
- [12] Cortes, J., Cespedes, E. R., and Miles, B. H. "Development of laser-induced breakdown spectroscopy for detection of metal contaminants in soils", Technical Report IRRP-96-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. NTIS No. AD A311 024, 1996.
- [13] B. Miles, J. Cortes, "Subsurface heavy-metal detection with the use of a laser-induced breakdown spectroscopy (LIBS) penetrometer system," *John Wiley & Sons, Inc. Field Analyt Chem Technol* 2: 75-87, 1998
- [14] J.D. Blacic, D.R. Pettit, and D.A. Cremers, "Laser-Induced Breakdown Spectroscopy for Remote Elemental Analysis of Planetary Surfaces," Published in

the Proceedings of the International Symposium on Spectral Sensing Research, Maui, HI, Nov. 15-20, 1992.

- [15] K.Y. Yamamoto, D.A. Cremers, L.E. Foster, and M.J. Ferris, "Detection of Metals in the Environment Using a Portable Laser-Induced Breakdown Spectroscopy (LIBS) Instrument," *Appl. Spectrosc.* 50, 222, 1996.
- [16] D. Cremers, M. Ferris, M. Davies, "Transportable Laser-Induced Breakdown Spectroscopy (LIBS) Instrument for Field-Based Soil Analysis" SPIE Proceedings, *Advanced Technologies for Environmental Monitoring and Remediation*, Vol. 2835, Nov. 1996.
- [17] B. DiGregorio, "Uncovering the Secret of the Rocks with LIBS", *Spectroscopy Showcase*, March 2003.
- [18] O. Graydon, "Homeland security drives LIBS forward", *Opto & Laser Europe*, Dec. 2003.
- [19] J. Morris, B. Forch, A. Miziolek, "A Novel Detector for Gas Chromatography Based on UV Laser-Produced Microplasmas" *Applied Spectroscopy*, Vol. 44, No. 6, 1990.
- [20] J. Simeonsson, A. Miziolek, "Spectroscopic Studies of Laser-Produced Plasmas Formed in CO and CO₂ using 193, 266, 355, 532 and 1064nm Laser Radiation," *Apply. Phys. B* 59, 1-9, 1994.
- [21] J. Thomason, "Spectroscopy Takes Security into the Field", *Photonics Spectra*, April, 2004.
- [22] A. Miziolek, K. McNesby, B. Homan, F. DeLucia, R. Harmon, R. Winkel, S. Grossman, A. LaPointe, N. Melikechi, R. Walters, "LINS: A New Versatile, Field Deployable, Real-Time Detector Systems for Force Protection and Anti-Terrorism Applications", 24th Army Science Conference, 2004.
- [23] K. Kincade, "LIBS Leaves the Lab for Field Work in Industry and Defense", *Laser Focus World*, Aug. 2003.
- [24] H. Kuzmany, "Solid-State Spectroscopy: An Introduction", Springer, p200, 1998.
- [25] W. Pierce, S. Christian, M. Myers, J.D. Myers, C. Hardy, J.A. Myers, R. Gadson, W. Younis, "Field testing for environmental pollutants using briefcase sized portable LIBS system," 3rd International Conference LIBS_2004, *Laser Induced Plasma Spectroscopy & Applications*, Malaga, Spain, Sept. 28 - Oct. 1, 2004.
- [26] N. Bloembergen, "Laser-Induced Electric Breakdown in Solids", *IEEE Journal of Quantum Electronics*, Vol. QE-10, No3, pp. 375-386, 1974.

- [27] J. Simeonsson, A. Miziolek, "Spectroscopic Studies of Laser-Produced Plasmas Formed in CO and CO₂ using 193, 266, 355, 532 and 1064nm Laser Radiation", *Applied Physics B* 59, 1-9, 1994.
- [28] C. DeMichelis, "Laser Induced Gas Breakdown: A Bibliographical Review", *IEEE Journal of Quantum Electronics*, Vol. QE-5, No. 4, pp. 188-202, April 1969.
- [29] R. Kowalewicz, E. Eberl, "Beam Profile Monitor for Pulsed CO₂-Laser", *IEEE Transactions on Plasma Science*, Vol. 24, No. 1. Feb. 1996.
- [30] K. Eland, D. Stratis, D. Gold, M. Angel, "Energy Dependence of Emission Intensity and Temperature in a LIBS Plasma Using Femtosecond Excitation", *Applied Spectroscopy*, Vol. 55, No. 3, 2001.
- [31] T. Namihira, S. Sakai, T. Yamaguchi, K. Yamamoto, C. Yamada, T. Kiyon, T. Sakugawa, S. Katsuki, "Electron Temperature and Electron Density of Underwater Pulsed Discharge Plasma Produced by Solid-State pulsed-Powered Generator", *IEEE Transactions on Plasma Science*, Vol. 35, No. 3, June 2007.
- [32] W. Schade, C. Bohling, K. Hohmann, D. Scheel, "Laser-Induced Plasma Spectroscopy for Mine Detection and Verification". *Laser and Particle Beams*, Vol. 24, pp. 241- 247, Cambridge University Press, 2006.
- [33] http://www.physics.nist.gov/PhysRefData/ASD/lines_form.html NIST, National Institute of Standards and Technology for the United States of America.
- [34] <http://www.arl.army.mil/www/default.cfm?Action=247&Page=250> ARL, US Army Research Laboratory.
- [35] H. Stosnach, "Environmental Trace-Element Analysis Using a Benchtop Total Reflection X-Ray Fluorescence Spectrometer", *Analytical Sciences*, Vol. 21, pp 873-876, July, 2005.
- [36] L. Lucia, B. Willett, J. Korppi-Tommola, "Laser-Induced Plasma Emission Spectroscopy (LIPS): A Useful Analytical Tool for the Surface Chemical Characterization of Coated Paper Materials", *BioResources* 1(1): pp. 75-92, 2006.
- [37] B. Fisher, H. Johnsen, S. Buckley, D. Haha, "Temporal Gating for the Optimization of Laser-Induced Breakdown Spectroscopy Detection and Analysis of Toxic Metals", *Applied Spectroscopy*, Vo. 55, No. 10, pp. 1312-1319, 2001.
- [38] http://www.appliedphotonics.co.uk/Libs/capabilities_libs.htm Applied Photonics Limited, Analytical Capabilities of LIBS.

- [39] <http://www.cee.vt.edu/ewr/environmental/teach/smprimer/icp/icp.html> Virginia Tech, Environmental and Water Resources Engineering, Inductively Coupled Plasma, ICP, Traci Bradford and M. Nicole Cook.
- [40] <http://www.stellarnet-inc.com> Porta-LIBS-2000 Instrument for Laser Induced Breakdown Spectroscopy data sheet, StellarNet, Inc. 2007.
- [41] W. Tawfik, Y. Mohamed, A. Asker, "Study of the Matrix Effect on the Plasma Characterization of Heavy Elements in Soil Sediments using LIBS with a Portable Echelle Spectrometer", Progress In Physics, Vo. 1, pp. 46-52, Jan. 2007.
- [42] R. Barbini, F. Colao, R. Fantoni, V. Lazic, A. Palucci, F. Capitelli, H. Van der Steen, "Laser Induced Breakdown Spectroscopy for Semi-Quantitative Elemental Analysis in Soils and Marine Sediments", EARSel-SIG-Workshop LIDAR, Dresden/FGR, June, 16-17, 2000.
- [43] V. Detalle, L. St-Onge, A. Hamel, R. Heon, M. Sabsabi, "Can the First Shots Make Sense In LIBS Analysis?" 3rd International Conference on Laser Induced Plasma Spectroscopy and Applications, Torremolinos, Malaga, Spain, Sept./Oct. 2004.
- [44] N. Eash, J. Lee, Y. Xhang, C. Jones, T. Ammons, "Laser-Induced Breakdown Spectroscopy (LIBS) for Quantitative Soil Analysis", International Annual Meetings of the American Society of Agronomy (ASA), Crop Science Society of America (CSSA), and Soil Science Society of America (SSSA), Nov. 4-8, 2007.
- [45] D. Alexander, D. Poulain, M. Ahmad, R. Kubik, E. Cespedes, "Environmental monitoring of soil contaminated with heavy metals using laser-induced breakdown spectroscopy", International Geoscience and Remote Sensing Symposium, IGARSS apos;94, Surface and Atmospheric Remote Sensing: Technologies, Data Analysis and Interpretation, Vol. 2, Issue 8-12, pp. 767-769, Aug. 1994.
- [46] S. Mirov, R. Pitt, A. Dergachev, W. Lee, D. Martyshkin, O. Mirov, J. Randolph, L. Delucas, C. Brouilledtte, T. Basiev, Y. Orlovskii, O. Alimov, "A Novel Laser Breakdown Spectrometer for Environmental Monitoring", Air Monitoring and Detection of Chemical and Biological Agents, SPIE Vol. 3855, pp.34-41, Sept. 1999.
- [47] A. Kumar, F. Yueh, J. Singh, S. Burgess, "Characterization of Malignant Tissue Cells by Laser-Induced Breakdown Spectroscopy," Applied Optics, Vol. 43, No. 28, Oct. 1, 2004.
- [48] M. Adamson, "LIBS for Detection of Trace Aluminum in Human Tissue Simulants," Wayne State University. Dept. of Physics, Published on-line <http://www.physics.wayne.edu/~srehse/LIBSonTissues.html>.

- [49] M. Baudelet, J. Yu, M. Bossu, J. Jovelet, J. Wolf, T. Amodeo, E. Fréjafon, P. Laloi, "Discrimination of Microbiological Samples using Femtosecond Laser-Induced Breakdown Spectroscopy" *Appl. Phys. Lett.* 89, 163903, 2006.
- [50] V. Lazic, F. Colao, R. Fantoni, V. Spizzicchino, "Recognition of Archeological Materials Under Water by Laser Induced Breakdown Spectroscopy" *Spectrochimica Acta Part B: Atomic Spectroscopy*, Vol. 60, Issues 7-8, pp.1014-1024, Aug. 2005.
- [51] K. Melessanaki, A. Mastrogiannidou, S. Chlouveraki, S. C. Ferrence, P. P. Betancourt, D. Anglos, "Analysis of Archaeological Objects with LMntI , a New Transportable LIBS Instrument", *LACONA V Proceedings, Lasers in the Conservation of Artworks*, Osnabrück, Germany, Sept. 15–18, 2003.
- [52] G. Cristoforetti, S. Legnaioli, V. Palleschi, L. Pardini, A. Salvetti, E. Tognoni, "Modi: A New Mobile Instrument for In Situ Standardless LIBS Analysis of Cultural Heritage", *Optical Methods for Arts and Archaeology*. Edited by Salimbeni, Renzo; Pezzati, Luca. SPIE, Vol. 5857, pp.129-138, 2005.
- [53] <http://www.arl.army.mil/www/default.cfm?Action=247&Page=249>, ARL, US Army Research Laboratory.
- [54] F. DeLucia, A. Samuels, et al., "Laser-induced breakdown spectroscopy (LIBS): a promising versatile chemical sensor technology for hazardous material detection." *IEEE Sensors Journal* 5(4): 681-689, 2005.
- [55] R. Harmon, F. De Lucia, et al. *The Use of Laser-Induced Breakdown Spectroscopy to Discriminate between Landmines and Other Objects*, 24th Army Science Conference Proceedings, 2004.
- [56] J. Almirall, S. Umpierrez, W. Castro, I. Gornushkin, J. Winefordner, "Forensic Elemental Analysis of Materials by Laser Induced Breakdown Spectroscopy (LIBS)", *Sensors, and Command, Control, Communications, and Intelligence (C3I) Technologies for Homeland Security and Homeland Defense IV*, SPIE Vol. 5778, pp. 657-666, May 2005.
- [57] J. Almirall, "A Novel LIBS system for Forensic Analysis of Materials", *Spectroscopy and Mass Spectrometry in Forensic Science II*, 34th Federation of Analytical Chemistry and Spectroscopy Societies Conference, Oct. 2007.
- [58] M. Sigman, C. Bridge, K. Vomvoris, and J. M. MacInnis, "LIBS: A New Tool for Forensic Analyses," in *Laser Applications to Chemical, Security and Environmental Analysis*, Technical Digest, Optical Society of America, 2006.
- [59] Y. Duan, Y. Su, et al. "A Field Portable Plasma Source Monitor for Real-Time Air Particulate Monitoring." *Anal. Chem.* 72(7): 1672-1679, 2000.

- [60] G. Zikratov, R. Vasudev, et al. "Laser Induced Breakdown Spectroscopy of Hafnium Doped Vitrified Glass." *Glass Technol.* 40(3): 84-88, 1999.
- [61] B. Castle, A. Knight, et al., "Battery Powered Laser-Induced Plasma Spectrometer for Elemental Determinations." *J. Anal. At. Spectrom.* 13(7): 589-595, 1998.
- [62] J. Singh, F. Yueh, et al., "Study of Laser Induced Breakdown Spectroscopy as a Process Monitor and Control Tool for Hazardous Waste Remediation." *Process Control Qual.* 10(3): 247-258, 1997.
- [63] K. Yamamoto, D. Cremers, et al. "Detection of Metals in the Environment Using a Portable Laser-Induced Breakdown Spectroscopy Instrument." *Appl. Spectrosc.* 50(2): 222-233, 1996.
- [64] D. Cremers, M.J. Ferris, et al., "Transportable Laser-Induced Breakdown Spectroscopy (LIBS) Instrument for Field-Based Soil Analysis." *Proc. SPIE-Int. Soc. Opt. Eng.* 2835(Advanced Technologies for Environmental Monitoring and Remediation): 190, 1996.
- [65] Y Deguchi et. Al., *Measurement Science and Technology*, "Industrial Applications of Temperature and Species Concentration Monitoring Using Laser Diagnostics", 13 R103-R115, 2002.
- [66] United States Food and Drug Administration, Center for Devices and Radiological Health, CDRH 1040.10 and American National Standards Institute ANSI 136.1 MPE level standards.
- [67] US Food and Drug Administration, Center for Devices and Radiological Health, CDRH 1040.10 and American National Standards Institute ANSI 136.1 MPE level standards
- [68] Kigre, Inc. MK-88 DPSS HESP laser, www.kigre.com